

**REACTIONS OF THE COMPLEXES $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$ (E=P,As or Sb)
AND $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L-L})\text{Cl}]$ (L-L= $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or $\text{Ph}_2\text{PCH}_2\text{PPh}_2$)
WITH A FEW HETEROALLENES, TERMINAL ACETYLENES (MONO/DI)
AND CARBONITRILES**

*A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY*

by
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practise of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE OF COURSE WORK

This is to certify that Anjali Krishna has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

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Chm 545 Principles of Inorganic Chemistry
Chm 632 Enzyme Reaction Mechan. and Enzyme Kinetics
Chm 800 General Seminar
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Chm 900 Ph.D. Thesis

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CERTIFICATE II

Certified that the work contained in the thesis entitled:
''Reactions of the Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$ (E = P, As
or Sb) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L-L})\text{Cl}]$ (L-L = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or
 $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with a few Heteroallenes, terminal Acetylenes
(mono/di) and Carbonitriles'' has been carried out by Anjali
Krishna under my supervision and that the same has not been
submitted elsewhere for a degree.



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PREFACE

One of the most exotic areas in which contemporary inorganic chemists could contribute profitably in the past hundred years has been the organometallic chemistry, a broad interdisciplinary field. Its sphere of study comprises all compounds wherein metal atom usually in a low valence state is bonded through carbon atom of an organic molecule, radical or ion. Since the time the Zeise salt (1848) and Victor Grignard's organomagnesium halides (1900) were synthesized and published, there have been spasmodic references related to the syntheses of a number of novel compounds like ferrocene, ruthenocene, etc. Subsequently the syntheses of the cyclopentadienyl transition metal complexes have given a new direction to the organic transition metal chemistry wherein a large number of new areas like homogeneous catalyses, etc have developed.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ was first prepared by Wilkinson (1969) and later on through a different facile route by Bruce and Windsor (1977). The pronounced steric interaction resulting from two bulky tertiary phosphines and the presence of high electron density on ruthenium in the complex have apparently been responsible for its much unusual chemistry. In addition the ready substitution of one of the PPh_3 molecules by other ligands, and/or the ease of scission of Ru-Cl bond in its methanolic solution has engendered an intense interest in its potential synthetic utility for a large

number of cationic and neutral substituted derivatives, and thereby making $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ as one of the most versatile organo-ruthenium(II) complex of contemporary interest. The work embodying the present thesis is also an attempt in the same direction.

The subject matter of chapter one reflects the scope and the objective of the work dealt in the thesis where the substitution reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ with a large number of other donor molecules like arsine, stibine, acetylenes, heterocyclic molecules, etc. have been examined. It also introduces, though very concisely, the present status of the ruthenium-cyclopentadienyl chemistry with particular emphasis on the aspects which have a bearing on the present work.

Chapter two describes the insertion reactions of carbonyl sulfide and carbon disulfide into ruthenium-hydride bond of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{H}]$ ($\text{E} = \text{P}, \text{As}$ or Sb) and $[(\eta^5\text{-C}_5\text{H}_5)\text{-Ru}(\text{L-L})\text{H}]$ ($\text{L-L} = \text{dppe}$ or dppm) which yield respectively monothioformato and dithioformato complexes. They have been characterized by elemental analyses and spectroscopic studies.

There are two parts of chapter three. The first part describes the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 1-Ethynyl pyrene which give cationic vinylidene and neutral η' -alkynyl complexes. The second part, embodies the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ with 1,7-octadiyne and 1,4-dicyano-2-butene wherein various cationic or neutral binuclear

products have been isolated. Tentative mechanism of the formation of these complexes have also been postulated on the basis of results of various physico-chemical studies.

Chapter four encompasses the synthetic procedures of mono and bi-nuclear, cationic complexes resulting from the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$; $\text{L}_2 = \text{dppe}$ or dppm) with 4-cyanopyridine and 4-cyanopyridine 1-oxide. Based on the results of various physico chemical studies, their tentative structures have also been proposed.

Chapter five deals with the cationic mono-and binuclear complexes which result from the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 1-piperidine carbonitrile and 1,4-piperazine dicarbonitrile in the presence of suitable anions. The structures of and bonding in the complexes have been proposed following the study of their physico chemical properties.

Chapter six has also been divided in to two parts. The first part concerns with the reactions between cyanamide or dicyanadiamide and $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm). The various binuclear and mononuclear cationic products have been characterised using the results of various physico chemical studies. The second part reports a new route for the one pot synthesis of a few literature reported cyano bridged cationic complexes as a result of reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{X}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X} = \text{Cl}$ or H) with 1,3,5-triazine.

A brief summary of the results of the work described in the thesis has been presented in chapter seven which also enumerates a few futuristic proposals for work.

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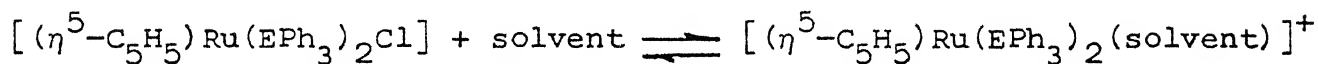
Chapter I

INTRODUCTION

I.1 Scope and Purpose

The ruthenium complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ ($\text{E} = \text{P, As, Sb}$; $\text{X} = \text{Cl, Br}$ etc.) are a few among the most studied molecules which have been recently synthesized (1969).¹ The rich variety of reactions besides their other unusual properties are rather fascinating. It has been well established that the complexes are the most attractive molecules for synthetic manipulations. In this direction excellent works of Bruce et al.,²⁻⁴ Treichel, et al.,⁵⁻⁷ Selegue, et al.,⁸⁻¹⁰ Davies et al.,¹¹⁻¹² Haines et al.,¹³ Wilczewski, et al.,¹⁴⁻¹⁵ and many others are most significant. The ready availability of the synthetic precursors and their congeners (prepared by ligand replacement at ruthenium) has led their reactions into other vast and interesting areas of organoruthenium compounds. It has been suggested that the enhancement of their chemical reactivity has been a result of relatively high electron density on the metal centre and the presence of two coordinated bulky PPh_3 molecules which lead to a great steric imposition. In

addition, the facile ionization of the chloro ligand and the easy substitution of EPh_3 (one out of the two molecules is lost very easily probably as a consequence of the steric bulk of the ligands) and further to their reactivities. The substitution reactions centred around Ru-Cl bond result in the replacement of chloride ion either by other anions or by neutral molecules to yield neutral or cationic complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ ($\text{X} = \text{anion}$) or $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{L}]^+\text{X}^-$ ($\text{L} = \text{neutral ligands}$). Presumably the formation of these products are based on the following equilibrium^{13,16-19} that lies largely to the right side in the polar solvents like CH_3OH , DMSO etc.



The second type of substitution reactions of these molecules involve the replacement of one of the EPh_3 molecules by other ligands like alkynes, heterocyclic molecules, etc. In addition there is also a third possibility of their reactions, though very little studied, which involves the cyclopentadienyl group. The latter reactions may determine the aromatic behaviour of the bonded C_5H_5 ring in complexes which could subsequently be related to the electron density on the metal centre, and also to the nature of the ligands attached to it.

The primary motive of our studies described in the thesis is to study the nature of substitution reactions at the metal centre in the $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L}_2)\text{X}]$ (L_2 = diphenylphosphinomethane or diphenylphosphinoethane) with a variety of potentially active small molecules like heteroallenes, N-heterocyclic bases, carbonitrile group containing ligands and terminal acetylenes. These reactions may lead to the synthesis of novel interesting complexes in an area which will not only make the chemistry of cyclopentadienyl-Ru(II) complexes more versatile, but these will also give a clue about the electronic and the steric effects influencing their syntheses.

The activation of heteroallenes by transition metal complexes is a topic of much current activity.²⁰⁻²² Among these the activation of small molecules like CO_2 , CS_2 have been extensively studied.^{21,23-36} Because of the wide spread interest in incorporating CO_2 into organic substrates and the paucity of successful examples of metal promoted CO_2 reductions,²⁰ the reaction of other heteroallenes like COS, CS_2 have also received considerable attention.³⁷⁻⁴¹ The most studied reactions of these have been those involving insertions into metal hydride bonds. Formal insertions of CO_2 and CS_2 into metal-hydride bond to form formato and dithioformato complexes are well known⁴²⁻⁵⁰ and have recently received much attention. This is because of their possible relevance to the catalyst of water gas shift reaction.⁵¹ Such a study

with COS, which is structurally similar to CO_2 and CS_2 , has been practically neglected despite its potentiality to yield various interesting products. Literature survey indicated very little data published in this direction.

There are hardly a couple of examples of COS insertion into a metal hydride bond to form monothioformato complexes. It is therefore thought that, it will be interesting to carry out a few reactions in this direction as an extension of our previous work, using substituted derivatives of hydride $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{H}]$ as precursors. These reactions could possibly lead to the isolation of some interesting monothioformato and dithioformato derivatives of ruthenium complexes containing $(\eta^5\text{-C}_5\text{H}_5)$.

Another interesting area which we considered worth probing into is that of reactivity of terminal acetylenes with $[(\eta^5\text{-C}_5\text{H}_5)\text{-RuCl}(\text{L}_2)]$. Although the field spanning the chemistry of transition metal alkylidene complexes is now well explored,^{4,57} it is only in the recent years that reliable synthetic procedures of metal complexes having unsaturated alkylidenes (vinylidene) and allenylidene have developed.^{4,8-10,54-59} But their chemistries still remain largely unexplored. The observation that the final products of these reactions have sometimes been dependent upon the nature of the acetylenic group has motivated us to initiate the work in this area. Consequently the reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{EPh}_3)_2]$ with a few monosubstituted and disubstituted terminal acetylenes have been

carried out, where acetylene-allene rearrangement has been shown to occur in one of the reactions.

Although a variety of synthetic organic reactions involving cyanamide and carbodiimide nitrogen as a nucleophile, have been reported,⁶⁰⁻⁶² very little work has been carried out so far related to the electrophilic attack by the metal ions/complexes on the terminal electron rich nitrogen atoms present in them. In continuation with the earlier work related to the exploitation of the nucleophilic character of the nitrogen atom of the metal bonded cyano group,⁶³⁻⁶⁶ we have studied the relative nucleophilicity of various nitrogen atoms present in carbodiimide in varying electronic environments. A study concerning the complexing properties of the nitrile group containing neutral organic molecules in non-aqueous medium has also been carried out. Thus the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ have been tried with ligands having N-C-N skeleton, like piperidine 1-carbonitrile and piperazine 1,4-dicarbonitrile. The interesting observation in these reactions has been that the carbonitrile moiety gets coordinated to the metal atom in the nitrile rather than in the -N=C=N form. Unlike cyanamide, a tautomeric equilibrium between $\text{>N-C}\equiv\text{N}$ and $\text{N}^+=\text{C}=\text{N}^-$ did not complicate the reaction path. We further studied the ligating properties of cyanamide and its dimer dicyanadiazide with cyclopentadienyl ruthenium complexes.

The interactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ with 4-cyanopyridine and its corresponding oxide have also been studied. Our primary motive in undertaking this study has been (1) to ascertain the relative donor capabilities of these ligands, (2) to investigate the nature of the metal orbital participation in back bonding with the low lying vacant π^* -orbitals of cyanopyridine and (3) to assess the influence of the asymmetric nature of cyanopyridine in synthesizing Ru(II) and/or polynuclear bridged complexes. The interest in these investigations which have received considerable attention in the past,⁶⁷⁻⁷² stems primarily from the existence of two potential coordination sites (nitrile and the pyridine nitrogens) raising a possibility of linkage isomerism. Not many suggestions have been made so far about the bonding behaviour of the bifunctional cyanopyridine. Therefore it becomes interesting to determine the site of coordination of ruthenium in the complexes.

With these aims under consideration we have carried out reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Cl}]$ or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Cl}]$ with a number of ligands. These have been described in the chapters enlisted below.

- (a) Chapter II : Insertion reactions of carbonyl sulphide and carbon disulphide into Ru-H bond of $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2]$ (E = P, As or Sb) and $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})]$ (L-L = dppe or dppm).

(b) Chapter III (Part I) : Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$
 (L = PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 =$
 dppe or dppm) with 1-Ethynyl pyrene.

(Part II) : Reactivities of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$
 (L = PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 =$ dppe
 or dppm) with 1,7-octadiyne and
 1,4-Dicyanobutene.

(c) Chapter IV: Syntheses and the study of the
 structural properties of mono and
 binuclear complexes obtained from the
 reactions of 4-cyanopyridine and
 4-cyanopyridine 1-oxide with $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ (L = PPh_3 , AsPh_3 ; $\text{L}_2 =$
 dppe or dppm) in the presence of
 suitable anions (PF_6^- or BPh_4^-).

(d) Chapter V : Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ (L =
 PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 =$ dppe or
 dppm) with piperazine 1,4-dicarbonyl
 nitrile and piperidine 1-carbonitrile
 in the presence of the anion (BF_4^- ,
 PF_6^- , BPh_4^- or ClO_4^-)

(e) Chapter VI (Part I): Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ (L =
 PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 =$ dppe or dppm)
 with cyanamide and dicyanadiazide.

Part II:

A new route for the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Ru}(\mu\text{-CN})\text{RuL}'_2(\eta^5\text{-C}_5\text{H}_5)]^+\text{X}^-$ ($\text{L}, \text{L}' = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2, \text{L}'_2 = \text{dppe}$ or dppm ; $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$ or BPh_4^-) using 1,3,5-triazine.

(f) Chapter VII:

A brief summary of the work described in the thesis. Futuristic work - plans have also been given in the same chapter.

It has been well established that the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ have fascinating chemistries, it is therefore appropriate to give a concise overview of the related work carried out so far on these molecules. The following section is an attempt in this direction.

During the past twenty years the chemistries of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L}_2)\text{Cl}]$ starting from the time of the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ by Wilkinson, et al., in 1969¹ have grown so vast, it is not possible to summarize all the work in a few pages of the thesis. Consequently a few arbitrary assumptions regarding the matter to be emphasized in a concise presentation of this nature have to be made. The versatility of these complexes as a synthetic precursor, is responsible for the vast volume of literature. As described earlier the variety of substitution reactions, these complexes undergo, is caused by high electron density at the metal centre and the ease of substitution of one of the EPh_3 molecules. Their chemistries can therefore be described

and classified in terms of the reactions which the different portions of the molecules undergo, under different reaction conditions, those related to Ru-Cl, Ru- η^5 -C₅H₅, Ru-L (L = PPh₃ etc) bonds.

I.2 Reactions at the metal phosphorus bond

The major driving force for these reactions is the lability of one of the PPh₃ molecules in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$, which can be substituted by a monodentate ligand. In addition there is also a possibility of substituting the second molecule of PPh₃ but this reaction takes place under stringent experimental conditions. Thus, a stepwise replacement occurs in the reaction with PMe₃ to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}]$ at 80-100°C and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{Cl}]$ at 110°C.^{5-7,73,74} Furthermore one or both PPh₃ molecules can be exchanged by dppe or dppm molecules depending on the reaction conditions. The substitution of PPh₃ by phosphites requires severe reaction conditions. Heating for a short period in decalin yields $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{P}(\text{OPh}_3)\}_2\text{Cl}]$ (R = Me or Ph).^{75,76} In the latter case some amount of the cyclometallated derivative has also been formed by the loss of HCl as a side product.⁷⁷ Some of these kind of reactions are listed in Table 1.1.

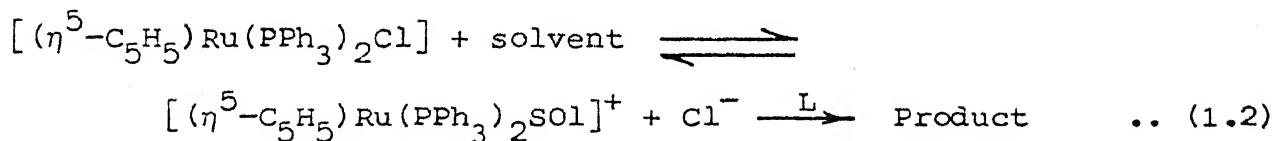
I.3 Reactions at Metal X bond (X = halide ion, CN⁻, NCS⁻ etc.)

(a) Metal-Cl bond

The chloride ion in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ can be replaced by

by other anionic, ligands (e.g. F^- , Br^- , I^- , H^- , CN^- , NCS^- etc.) to yield thermally stable products.^{13-14,78,79} The hydride derivative of the phosphine complex is obtained by reacting its corresponding chloro complex with $LiAlH_4$.⁷⁹ A convenient and facile route to synthesize hydride⁷⁶ $[(\eta^5-C_5H_5)RuLL'H]$ ($L, L' = PPh_3$, dppm, dppe, $L = PPh_3$, $L' = CO$, $CNBU$) was described by Chatt and Shaw⁸⁰ using alcoholic base. These hydrides react with chloroform or CCl_4 to give chlorides, with CS_2 , to form η' -dithioformato complexes. Some of them enter into chelation, e.g., $[(\eta^5-C_5H_5)Ru(S_2CH)(PPh_3)]$.⁷⁶

Alkyl complexes have been prepared by treating appropriate organolithium reagents RLi with the phosphine complex, e.g. ($R=Me$, $C_6F_5^-$).⁷⁹ Bright yellow complexes of trichlorostannate $[(\eta^5-C_5H_5)Ru(PR_3)_2SnCl_3]$ ^{6,79} ($R=Me$ or Ph) have been synthesized by the insertion of $Sn(II)$ chloride into $Ru-Cl$ bond. The formation of these complexes occur by the facile displacement of weakly bound solvent molecule from the solvated cation.^{13,16-19}



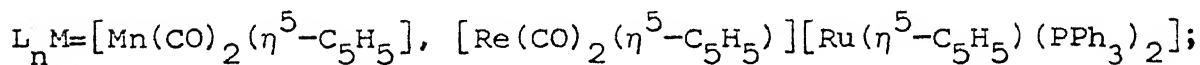
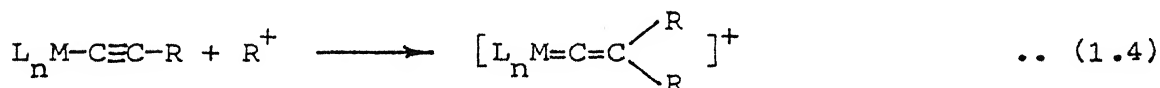
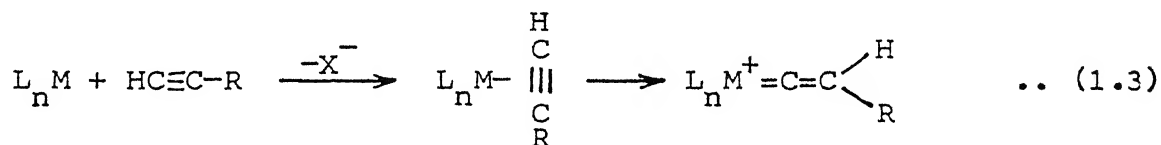
(b) Synthesis of η' -Vinylidene, η' -propadienyldiene, η' -acetylides and their reactions

Synthesis of η' -vinylidenes

Vinylidenes (methylene carbene) $:C=C \begin{matrix} \nearrow R \\ \searrow R \end{matrix}$, which are unstable

in free state, form stable complexes with transition metal ions. They may be classified as two electron donors and act as terminal or bridging ligands.⁸¹

Terminal acetylene (1-alkynes) complexes undergo a 1,2-hydrogen shift to give vinylidene complexes^{3,55,56} proceeding via an intermediate η^2 -alkyne complex which has been isolated or detected spectroscopically in some cases.^{3,82-84} Protonation or alkylation of several ethynyl metal derivatives gives the corresponding complexes in high yields.^{56,85} It is a convenient route for the synthesis of disubstituted vinylidene complexes as well as the parent compounds, which can not be obtained from 1-alkynes.

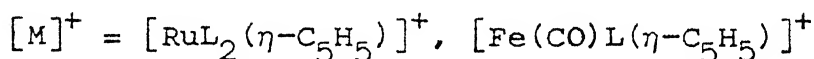
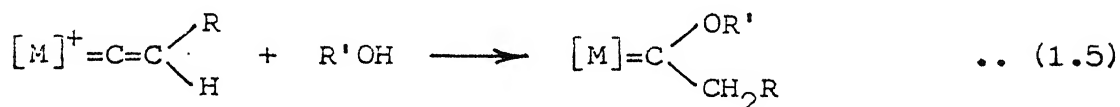


X = solvent, halide or CO .

The electron distribution on the vinylidene ligand in the complex (electron deficiency on α -carbon and a considerable electron density on the β -carbon) renders α -carbon susceptible to nucleophilic attack and β -carbon, to electrophilic attack. A few of the reactions are described below.

Nucleophilic Addition to the α -Carbon

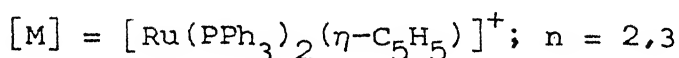
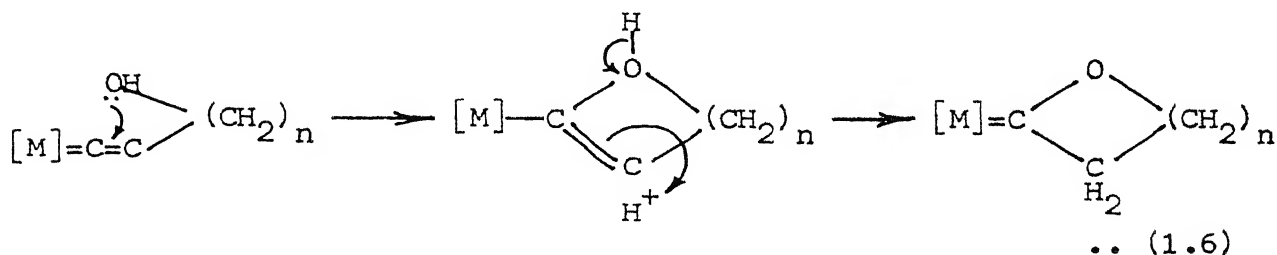
Alkoxy (alkyl) carbene complexes are formed more or less rapidly by reacting alcohols with cationic vinylidene complexes.^{56,86,87} The addition follows the expected direction to give conventional Fisher type carbene complexes.



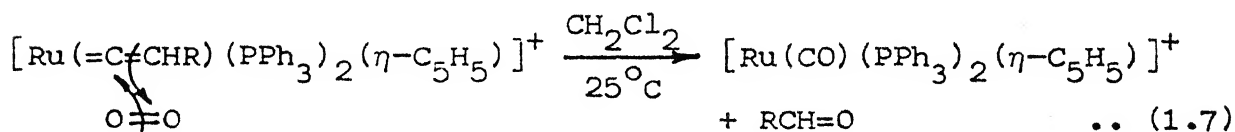
It has also been observed qualitatively that the variation in reactivity is a combined effect of steric and electronic factors. Bulky ligands protect the α -carbon from attack, and the rates of formation of the alkoxy carbene complexes are inversely proportional to the cone angle of the L in $[(\eta-C_5H_5)Ru(PPh_3)L]CO$ (cone angle ca 95°) \sim $CNBU^t$ (ca 95°) $>$ $P(OMe)_3$ (107°) $>$ PMe_3 (118°) $>$ PPh_3 (145°). A good agreement is found between this reactivity and Tolman's⁸⁸ electronic factors which predict the reactivity order, $CO > P(OMe)_3 > (CNBU^t) > PPh_3 > PMe_3$.

An increase in electron withdrawing power of the vinylidene substituents R, ($:C=CHR$), enhances the reaction rate, as has been found with the series, $R=CO_2Me > Ph > Me$. The reactivity decreases⁵⁶ with the nature of the reacting alcohols $R'OH$ ($MeOH > EtOH > Pr^iOH$).

Rapid intramolecular addition of an alcohol function occurs to the supposed intermediate (vinylidene complex) in the reaction of $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{OH}$ with metal halide complexes⁵⁵ yielding the cyclic carbene complexes.



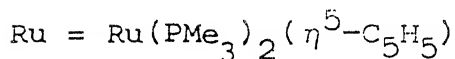
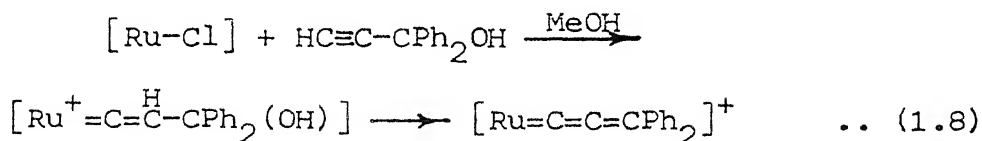
One of the most interesting reactions of cationic vinylidene complexes is with dioxygen, yielding a carbonyl cation and the corresponding aldehyde.⁸⁷



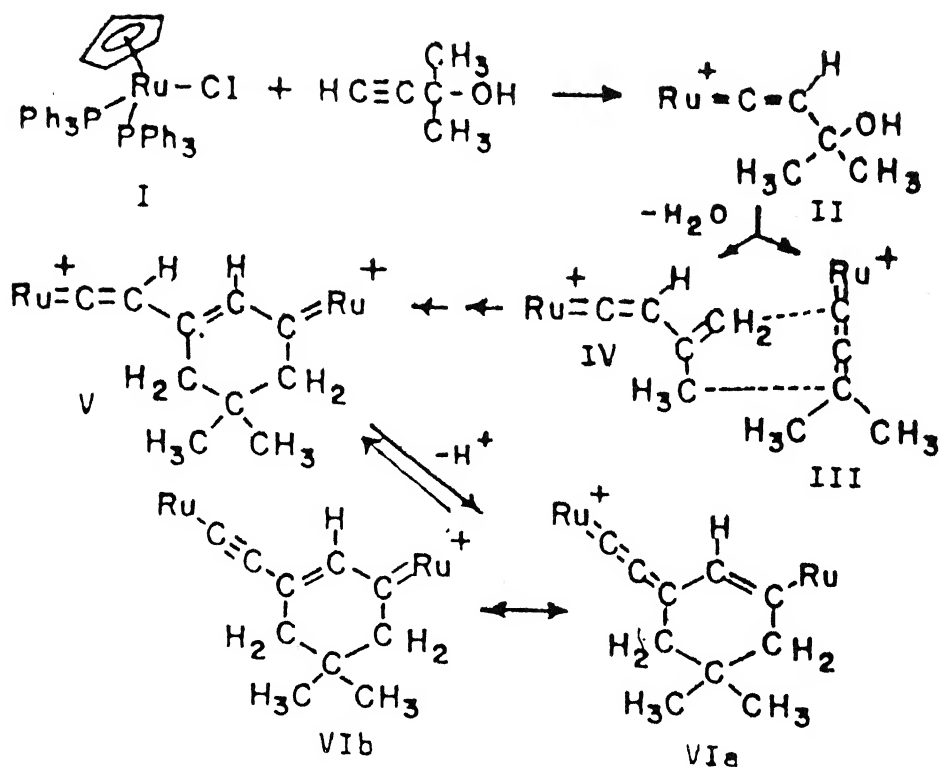
Synthesis of Propadienyldene (Allenylidene) Complexes

A general route to complexes containing propadienyldene ligand is by the loss of (1) water or alcohols from suitable carbene or vinylidene precursors, (2) oxo or alkoxy functions from ynolate anions. The latter are generally obtained from reactions of alkyne complexes containing an ester group, like

methylpropiolate. Vinylidene complexes containing hydroxyl groups on the γ -carbon can be readily converted to the propadienylidene derivative by the loss of one water molecule.^{8,9} These reactions are promoted by a base, or by using COCl_2 or CSCl_2 . For example,



Attempts to prepare the dimethyl analog from $\text{HC}\equiv\text{CMe}_2(\text{OH})$ led to the formation of binuclear vinylidene-carbene complex $[(\eta^5-\text{C}_5\text{H}_5)_2(\mu-\text{C}_{10}\text{H}_{12})(\text{PPh}_3)_2](\text{PF}_6)_2$.⁸ The reaction takes place through the formation and deprotonation of the complex shown in Scheme I.1. Remarkable regioselectivity is demonstrated in the formation of the two new carbon-carbon bonds. Most probably the alkynol reacts with ruthenium chloride (dissociated in methanol)^{13,17} to yield an intermediate hydroxy vinylidene complex(II), which spontaneously dehydrates to a dimethyl allenylidene cation (III), an isopropenylvinylidene cation (IV) or both. Presumably these reactions take place through the bond formation between the two δ -carbons of IV (which should be nucleophilic at least upon



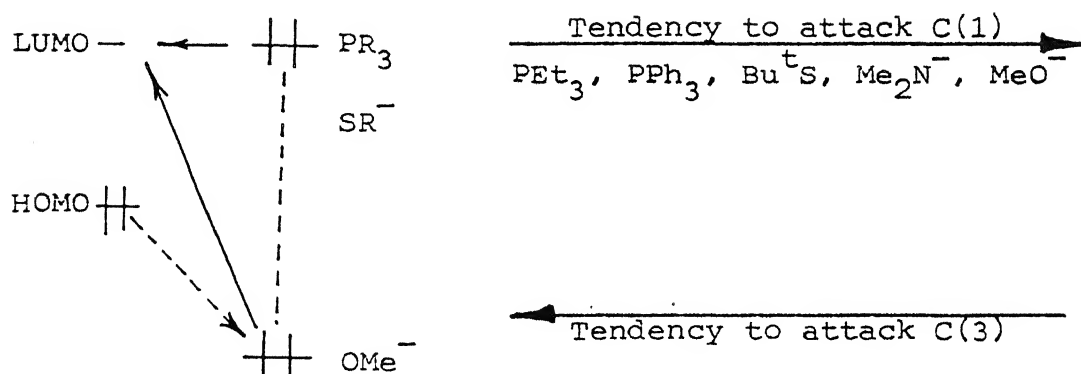
Scheme I.1

deprotonation),^{89,90} and the α - and γ -cations of **III** (which should be electrophilic)⁹¹⁻⁹³ probably in a stepwise manner.

Reactions

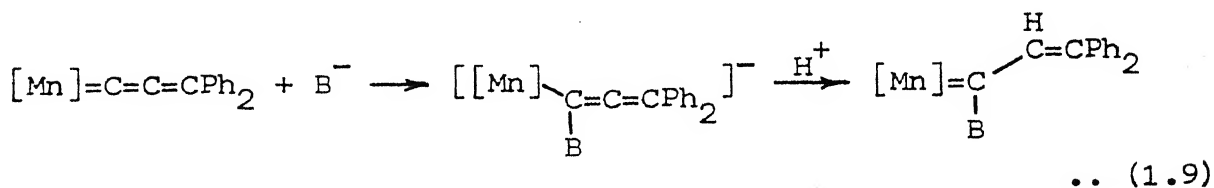
The reactivity of allenylidene complexes is rationalised by considering the nature of the HOMO and the LUMO of the $M=C=C=C$

fragment.⁹⁴ Nucleophilic reagents can be classified according to whether they add to C(1) or C(3):

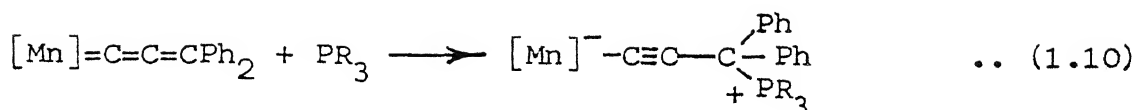


Highly electronegative donor bases (methoxide, etc.) have low lying lone pair of electrons and can interact with the HOMO, whereas tertiary phosphines have high energy donor orbitals which interact directly with the LUMO.

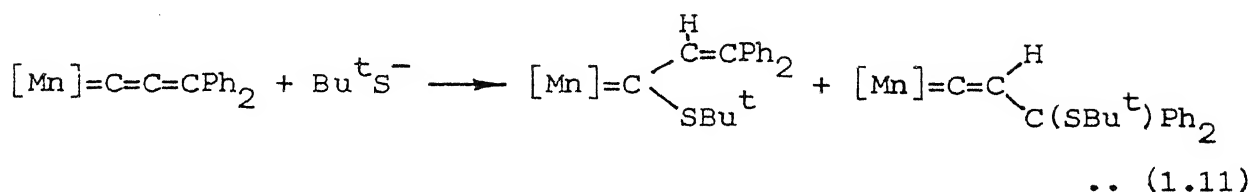
In conclusion, anionic reagents like methoxide or amide add to C(1) and afford vinyl carbene complexes after protonation e.g.,



Reactions of tertiary phosphines afford Zwitterionic phosphonium salts by addition to C(3):

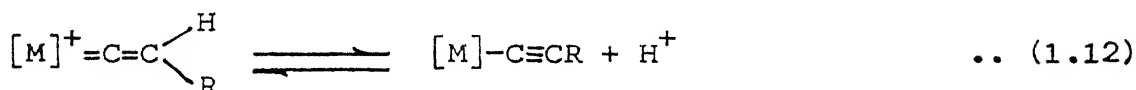


t-Butylthiolate anion attacks both the sites giving both the types of products:

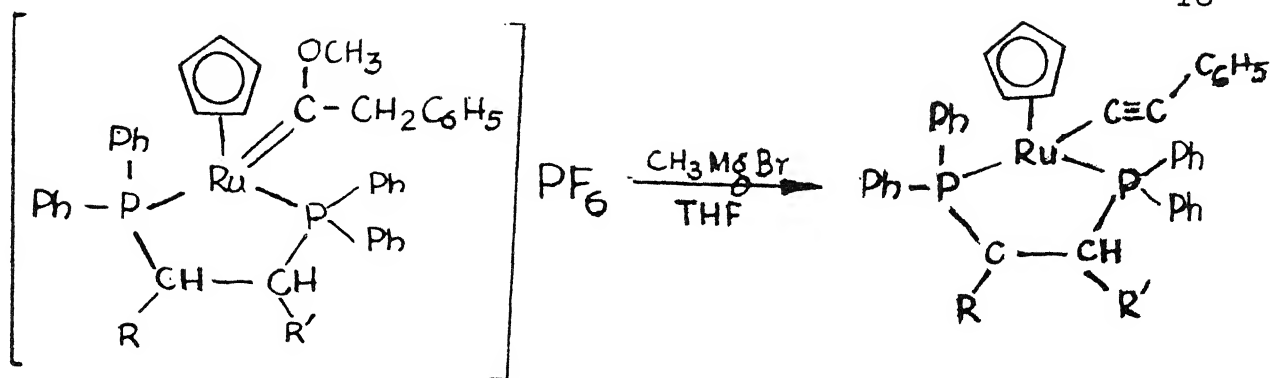


Synthesis of η' -Acetylide Complexes

Cationic vinylidene complexes bearing β -hydrogen are rapidly deprotonated to give the corresponding neutral η' -acetylide complexes.



The bases used were hydroxide, alkoxide, carbonate ions, alkyl lithium, NaBH_4 or alumina.⁸³⁻⁸⁵ The reaction is the reverse of the vinylidene synthesis by protonation of η' -acetylide, and the two complexes form a simple acid base system. In a few cases alkoxy carbene complexes of cyclopentadienyl ruthenium could be converted to the corresponding acetylide using CH_3MgBr .

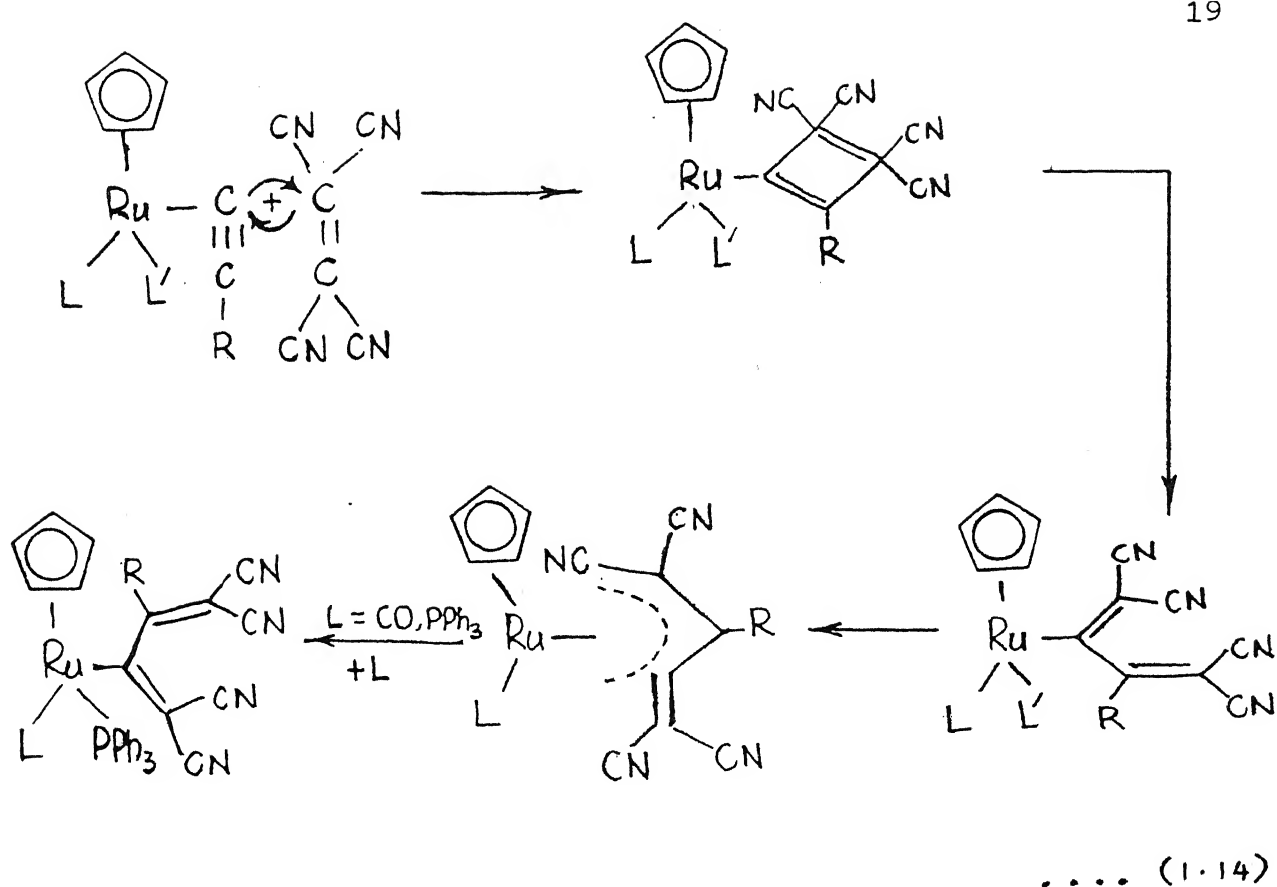


.. (1.13)

Reactions of η^5 -Acetylides

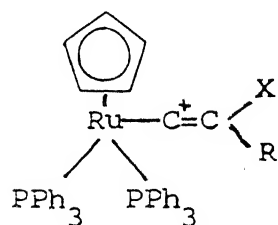
A wide range of complexes of the type $[(\eta^5-\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)-(\text{C}\equiv\text{CR})\text{L}]$ ($\text{L} = \text{CO}, \text{CNBu}^t, \text{PR}_3, \text{P(OR)}_3$)]^{56,73,84,95} could be synthesised by ligand exchange reactions.

The acetylide complexes in which β -carbon is generally electron rich, behaves like a nucleophile towards reagents such as H^+ , Me^+ and Et^+ ,^{85,96} alkyl halides, electrophilic olefins.^{97,98} Reactions of tetracyanoethylene with $[\text{Ru}(\text{C}_2\text{R})\text{L}_2(\eta^5-\text{C}_5\text{H}_5)]$ $\text{R}=\text{Me}, \text{Ph}$; $\text{L}_2=(\text{PPh}_3)_2, (\text{CO}, \text{PPh}_3)$ or dppe proceed via paramagnetic intermediates and a combination of cycloaddition and ring opening processes to give a range of cyclobutenyl, butadienyl and allyl complexes.⁹⁸

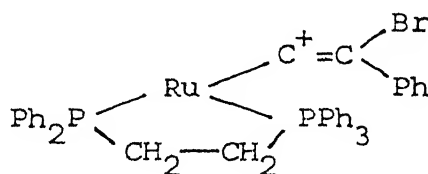


Similar reactions have been carried out between η' -acetylides complexes and various substituted styrenes like $4\text{-RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})_2$ ($\text{R}=\text{NO}_2, \text{H}, \text{NMe}_2$) to give allylic, butadienyl and cyclobutenyl complexes.⁹⁷

Addition of halogen (Cl_2 , Br_2 or I_2) to η' -acetylides have yielded cationic halovinylidene derivatives.^{99,100}



(a)

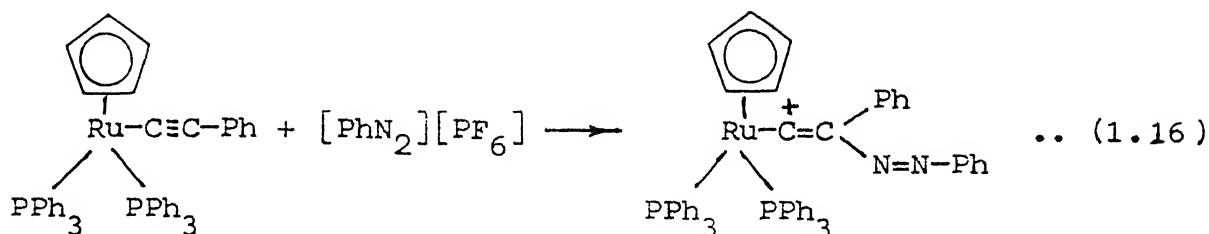


(b)

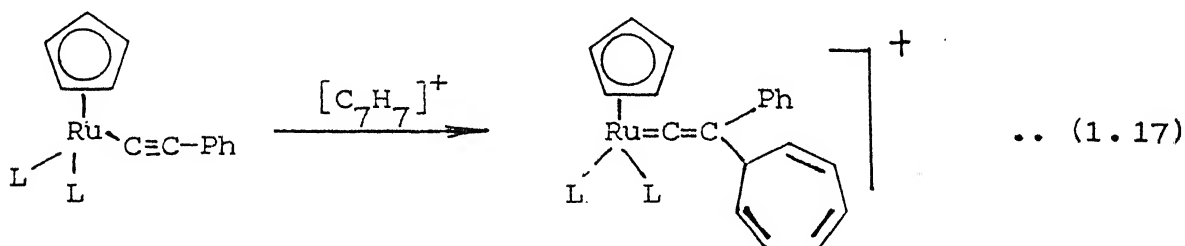
.. (1.15)

($\text{X} = \text{I}, \text{Br}, \text{Cl}$; $\text{R} = \text{Ph}, \text{Me}$)

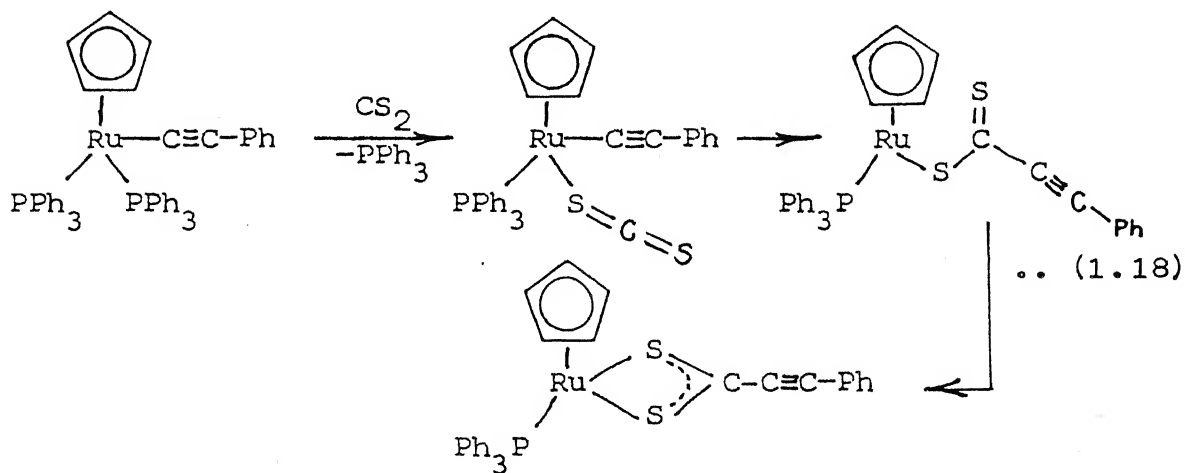
Ruthenium ν acetylides also react with electrophilic aryldiazonium cations to give their corresponding aryldiazovinylidene complexes.^{101,102}



Addition of tropylium salts of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}_2\text{Ph})]$ ($\text{L} = \text{PPh}_3$, $\text{L}_2 = \text{dppe}$) has given the cationic cycloheptatrienyl vinylidene complexes.¹⁰¹



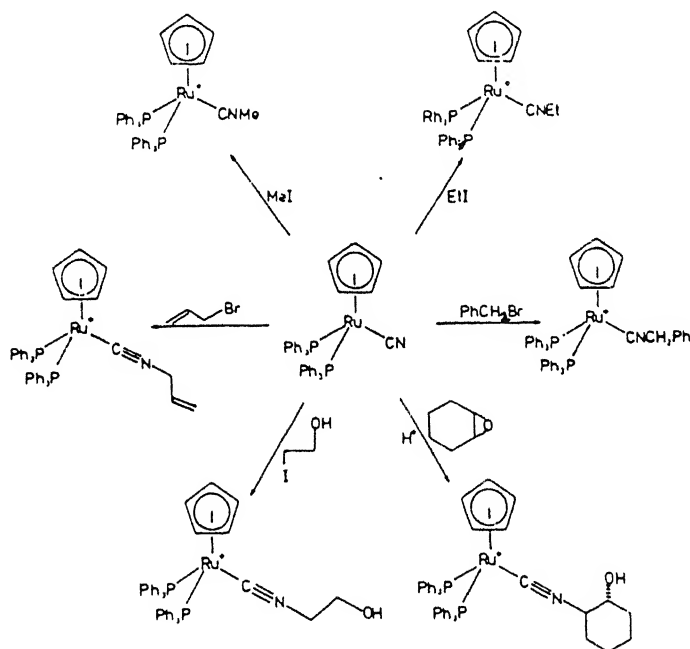
Recently Bruce, et al. have reported formal insertion of CS_2 into $\text{M-C}(\text{SP})$ bond of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2]$.¹⁰³



$C \equiv C$ triple bond of the acetylide complexes readily form 1:1 adducts with copper (I) chloride,^{18,74} and other suitable metal derivatives.

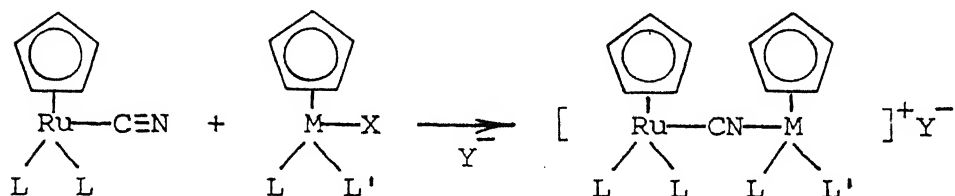
(c) Metal-CN Bond

The cyano complexes $[Ru(\eta^5-C_5H_5)(PPh_3)_2CN]$ can be protonated or alkylated. It also reacts with BPh_3 to give $[(\eta^5-C_5H_5)Ru(PPh_3)_2(CNBPh_3)]$.¹³ Interesting conversions from coordinated cyano group to isonitriles have been carried out by the nucleophilic reactions using RI ¹² ($R = Me, Et, CH_2CHCH_2, PhCH_2$, etc. (Scheme I.2).



Scheme I.2

Another interesting reaction of the cyano complexes is the formation of bimetallic cyano-bridged cations by treating the former with suitable organometallic halogeno complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{-M}(\text{LL}')\text{Cl}]$ ($\text{M} = \text{Fe}$; $\text{L}, \text{L}' = \text{dppe}$; $\text{M} = \text{Ru}$; $\text{L} = \text{PPh}_3$) (Scheme I.3).¹¹



M	L ₂	L, L'	X	Y
Ru	(PPh ₃) ₂	(PPh ₃) ₂	Cl	PF ₆
Fe	(PPh ₃) ₂	dppe	Br	PF ₆

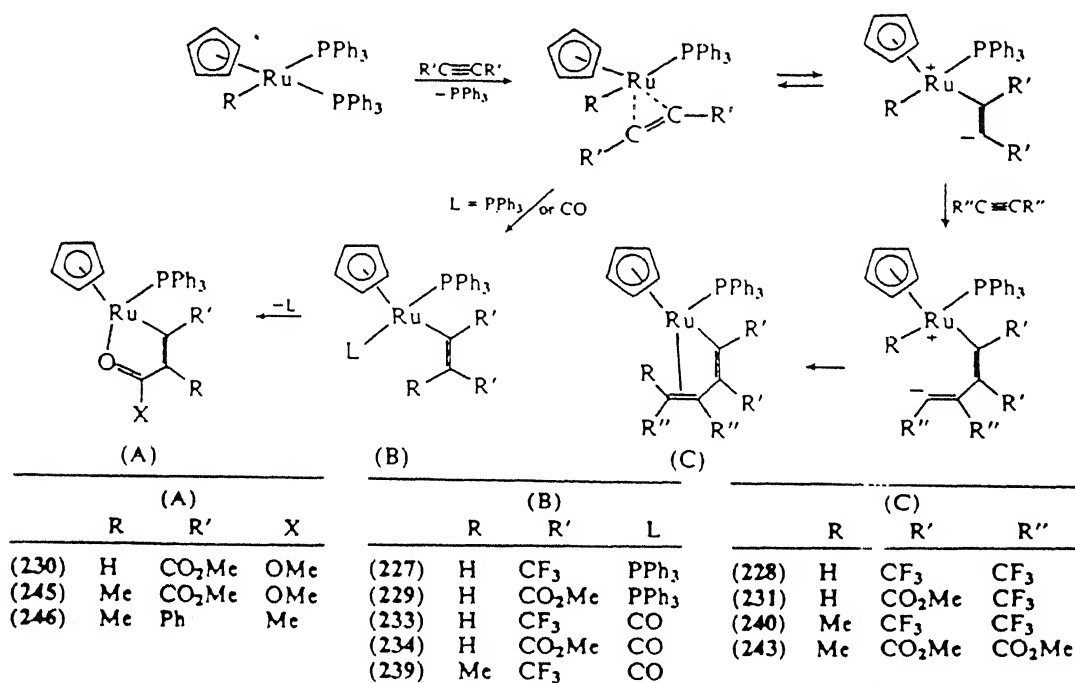
Scheme I.3

Metal-R Bond (R=H or alkyl group)

The alkyl derivatives undergo intramolecular cyclometallation reactions by losing the alkyl group to form $[(\eta^5\text{-C}_5\text{H}_5)\text{-Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)]$.^{75,77} Alkyl complexes react with azobenzenes readily to form dark green 2-(phenylazo)phenyl complexes.⁷⁷

Another class of reactions belonging to this category are those which take place between hydrido complexes and electron deficient olefins and alkynes. These reactions yield a variety of interesting products. Thus, the reaction with $(\text{CF}_3)\text{C}=\text{C}(\text{CN})_2$ gives a

complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{C}(\text{CN})_2\text{CH}(\text{CF}_3)_2\}(\text{PPh}_3)_2]$.¹⁰⁵ Alkynes having electronegative substituents give complexes by the insertion and cyclization process (Scheme I.4).



Scheme I.4

The reactions between terminal or substituted alkynes and the hydrido complexes yield oligomeric products^{105,106} (Scheme I.5). In some cases, η' -acetylide derivatives are also isolated, e.g.

methyl propiolate.¹⁰⁷ Alkyl ruthenium complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{R}]$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$) form similar diverse range of products in their reactions with alkynes (Scheme I.4).

Several substrates are deprotonated by basic moiety $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Me}]$ with a loss of methane molecule.¹⁰⁷ A novel highly unsaturated alkyne trimer 1,3,4,5-tetraenyl complex¹⁰⁶ is formed by the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Me}]$ with trifluoropropyne.

Reactions of $\text{Ru}-(\eta\text{-C}_5\text{H}_5)$

The cyclopentadienyl group of the complex(I) can be readily substituted by the three monodentate ligands and particularly in the presence of oxidizing agents like NOX ($\text{X} = \text{Cl}, \text{Br}, \text{Br}_3$) to yield Ru(II) octahedral complexes.^{108,109} Thus, these complexes react with NOX yielding $[\text{Ru}(\text{NO})(\text{EPh}_3)_2\text{Cl}_3]$. The SnCl_3 derivatives of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ yield $[\text{Ru}(\text{PPh}_3)(\text{NO}_2)\text{SnCl}_3-(\eta\text{-C}_6\text{H}_5\text{-PPh}_2)]$ in which one of PPh_3 is π -bonded with ruthenium.¹⁰⁹ In the presence of substituted azobenzenes like decafluoroazobenzene the complex undergo intramolecular cyclometallation with cyclopentadienyl ring.⁷⁷

Metal π -Triphenylphosphine and Tetraphenylborate Sandwich Complexes

I.R. spectroscopy and X-ray crystal structure determination

unrevealed the mysteries of the compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{BPh}_4)]$,¹¹⁰ obtained by the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ with NaBPh_4 . The novel structure having π -bonded phenyl ring as proposed by i.r. studies,¹¹⁰ is corroborated by X-ray studies.¹¹¹ This has a half-sandwiched Zwitterionic $\text{Ru}(\text{II})$ structure as shown in Fig. I.1a. Literature survey reveals several other interesting examples (Fig. I.1b,c,d) which fall in this category.^{15,112,113}

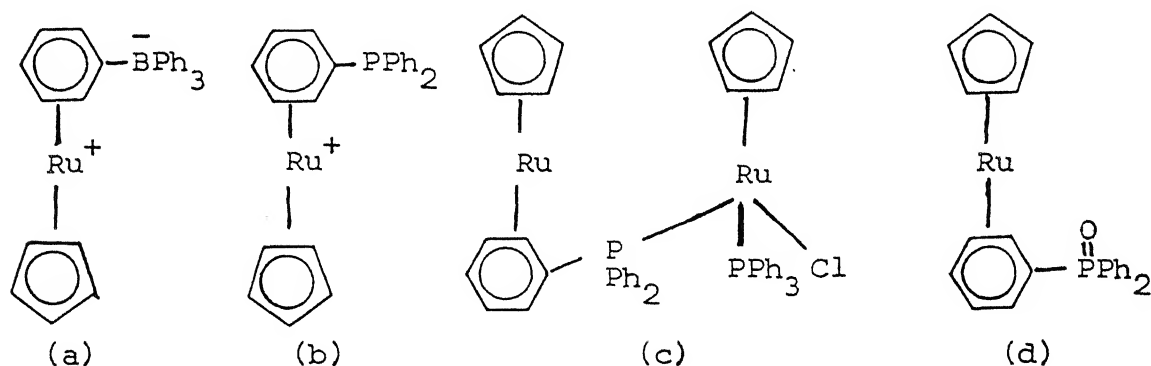
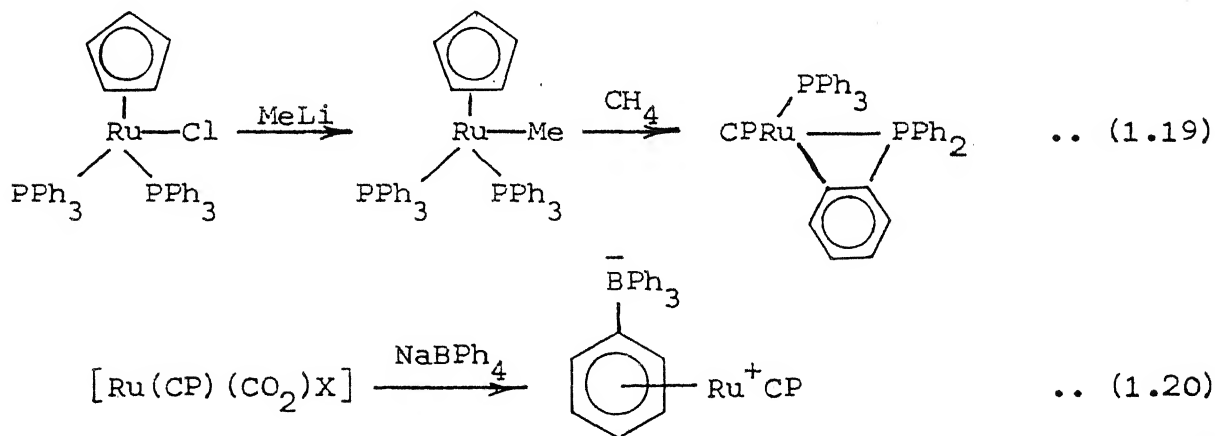


Fig. I.1

These compounds are unique in many ways exhibiting their own characteristic properties. They have been found to be highly useful in synthetic organic chemistry.



Literature survey however indicates that in all these reactions emphasis has been given to the reactions with unsaturated organic compounds and their derivatives resulting in the formation of some unusual π - and σ bonded complexes.^{105,106,114}

It is thus clear from this concise review that the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ but have also given to chemists an opportunity for future work by providing a deeper insight into the electronic and steric factors which play an important role in these reactions.

Most of the interesting reactions using $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{X}]$ are enlisted in Table 1.1.

Table 1.1 Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ and other closely related complexes

S.No.	Reactants	Reagent/ solvent	Products	Reaction conditions	Ref.
1	2	3	4	5	6
1.	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{C}_5\text{H}_6$	Ethanol	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$	Refluxed for two hours	78
2.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}] + \text{AsPh}_3$	Benzene	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{AsPh}_3)_2]$	Refluxed for 48 hours	76,79,1
3.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}] + \text{PMe}_3$	Pet.Ether	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)(\text{PMe}_3)]$	-	5,6,74
4.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}] + [\text{P(OPh)}_3]$	Decalin	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)(\text{P(OPh)}_3)]$	Refluxed for 2 minutes	76
5.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2] + (\text{L-L})$ (L-L = dppe or dppm)	Benzene	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})\text{Cl}]$	Refluxed for 8-10 hours	116
6.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{EPh}_3)_2] + \text{NaOMe}$ (E = P, As)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\text{PPh}_3)_2]$	Refluxed for 15 minutes	76
7.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{NH}_4\text{F} + \text{NaHCO}_3$	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuF}(\text{PPh}_3)_2]$	Refluxed	77
8.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{KX}$ (X = Br, I, CN, NCS etc.)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuX}(\text{PPh}_3)_2]$	Refluxed for 1-3 hours	14,79

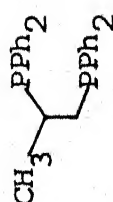
..contd.

Table 1 (contd.)

1	2	3	4	5	6
9.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{SnCl}_2$	1:1 Benzene/ Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SnCl}_3)(\text{PPh}_3)_2]$	Refluxed for 1-3 hours	6, 79
10.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuX}(\text{PPh}_3)_2] + \text{L}$ (L=Py, 7-pic; X=Cl, Br, I, CN, NCS and SnCl_3)	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L})(\text{PPh}_3)\text{X}]$	Refluxed for a few hours	117
11.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{L-L} + \text{Y}^-$ (L-L=bipy, o-phen, nbd, en etc.) Y = PF_6^- , BF_4^-	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L-L})]^+\text{Y}^-$	Refluxed for several hours	112, 117
12.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{LiR}$ (R = Me, CH_2Ph , Et, C_6F_5)	Benzene and Ether	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{R}]$	Stirred for 45 minutes	106, 118
13.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{Fe}_2(\text{CO})_9$	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PPh}_3)\text{Cl}]$	Stirred at 60°C for 23 hours	79
14.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{PMe}_3 + \text{PF}_6^-$	CH_3CN	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_3]^+\text{PF}_6^-$	Kept at 60° and 110° in a sealed tube	75
15.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{P(OMe)}_3 + \text{PF}_6^-$	Decalin	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{P(OMe)}_3\}_3]^+\text{PF}_6^-$	Refluxed for 4 hours	75
16.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{dtc}/\text{S}_2\text{C-Z}$ (Z = OMe, OEt, NEt ₂ , $-\text{N}(\text{CH}_2)_4$, H)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{S}_2\text{C-Z})\text{Cl}]$	Refluxed for few hours	14, 76
17.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{L} + \text{NH}_4^+\text{PF}_6^-$ (L = ClCH_2CN , $\text{CH}_2=\text{CHCN}$, PhCN etc.)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{L})]^+\text{PF}_6^-$	Refluxed for 1-3 hours	75

..contd.

Table 1 (contd.)

1	2	3	4	5	6
18.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2 + \text{L} + \text{NaBPh}_4$ ($\text{L}=\text{NC}(\text{CH}_2)_2\text{CN}$, $1,3\text{-C}_6\text{H}_4(\text{CN})_2$, $1,4\text{-C}_6\text{H}_4(\text{CN})_2$ etc.)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2]^{1/2}[\text{BPh}_4]$	Refluxed	75
19.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{C}_5\text{H}_6$	-	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}]$	-	14,15
20.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] +$ Ethylene glycol + NaBPh ₄	-	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)\text{PPh}_2 -$ $(\eta\text{-C}_6\text{H}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_5)]\text{BPh}_4$	Refluxed for 1 minute	15
21.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{NaClO}_4$	-	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_6\text{H}_5\text{Ph}_2\text{PO})] -$ ClO_4	Passed O ₂ for 45 minutes	112
22.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{NaBPh}_4$	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_6\text{H}_5\text{BPh}_3)]$	Under boiling conditions	110
23.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] +$ $2\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$	Petroleum Ether	$[\text{Ru}(\eta^2\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2) -$ $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$	Under refluxing conditions	119
24.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{MeOCS}_2\text{K}$	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{S}_2\text{COME}(\text{PPh}_3))]$	Refluxed for two hours	120
25.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] +$ $\text{Ti}[\text{C}_5(\text{COOMe})_5]$	Aceto- nitrile	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe}(\text{PPh}_3)_2) -$ $[\text{C}_5(\text{COOMe})_5]$	Stirred at room temperature	121
26.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] +$ $\text{Ti}[\text{C}_5(\text{CO}_2\text{Me})_5]$	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\eta\text{-C}_5(\text{COOMe})_5\}]$	Stirred at 60°C for two hours	121
27.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] +$  or $(\text{CH}_3)\text{dpppe}$	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}\{(\text{CH}_3)\text{dpppe}\}]$	Refluxed for 4 hours	122

..contd.

Table 1 (contd.)

1	2	3	4	5	6
28.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuLL'R}] + \text{SO}_2$ LL' = CO, PPh ₃ ; R = Me, PhCH ₂	Chloroform	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}(\text{PPh}_3)_2\text{SO}_2\text{R}]$	Refluxed for two hours	123
29.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] + \text{RI} + \text{NH}_4\text{PF}_6$ (R = CH ₂ Ph, Me, Et, -CH ₂ CH ₂ OH etc.)	CH ₂ Cl ₂	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{CNR})]\text{PF}_6$	Stirred at room temp.	12
30.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] +$ $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2'\text{X}] + \text{NH}_4\text{PF}_6$ (M=Fe or Ru; L ₂ '=(PPh ₃) ₂ or dppe)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2'\text{Ru}(\mu\text{-CN})\text{ML}_2']$ $(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$	Stirred at 50°C for two hours	11
31.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Me})(\text{PPh}_3)_2]$	-	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2) - (\text{PPh}_3)]$	Intramolecular cyclometallation	77
32.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{P}(\text{OPh})_3\}_2\text{Cl}]$	Decalin	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{C}_6\text{H}_4\text{OP}(\text{OPh})_2\} - \{\text{P}(\text{OPh})_3\}]$	Under refluxing condition	76, 77
33.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PMe}_3)_2] + \text{L}$ + NH ₄ PF ₆ (L = CH=CHPh, CH ₂ =CHCN, CH=CHCH ₃ , trans-ClCH=CHCl, PhC≡CPh, MeO ₂ C-C≡C-CO ₂ Me)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{L}]\text{PF}_6$	Under refluxing condition	73, 84
34.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})\text{Cl}] + \text{L} + \text{NH}_4\text{PF}_6$ (L = C=C-R; R = Me, Et)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})\text{L}]\text{PF}_6$	-	75

..contd.

Table 1 (contd.)

1	2	3	4	5	6
35.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}] + \text{HC}\equiv\text{CR}$ + NaBF_4 , NaBPh_4 or NH_4PF_6 (R = Me, Ph, CO_2Me , C_6H_5 ; $\text{L}_2 = (\text{PPh}_3)_2$ or dppm)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}_2\text{HR})]^+\text{X}^-$ (X = PF_6^- , BF_4^- or BPh_4^-)	Heated under reflux for 10 minutes	84
36.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}_2\text{HR})]^+\text{X}^- + \text{NaOMe}$ L_2 and R same as in 35	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L}_2)(\text{C}_2\text{R})]$	-	84
37.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}_2\text{HR})]^+\text{X}^-$ + $(\text{R}_3'\text{O})\text{PF}_6$ $\text{R}' = \text{Me}$ or Et L_2 and R same as in 35	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L}_2)(\text{C}=\text{CRR}')]\text{PF}_6$	Stirred for 1/2 hour	56, 95
38.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{HR})]^+\text{PF}_6^-$ (R = Ph, Me) L_2 and R same as in 35	MeOH	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L})-$ $\{\text{C}(\text{OR}')\text{CH}_2\text{R}\}]\text{PF}_6$ (L = PPh_3 , CO; $\text{R}' = \text{Me}$, Et)	Under refluxing conditions	56
39.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppm})\text{Cl}] + \text{HC}\equiv\text{C-Ph}$	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppm})-$ $\{\text{C}(\text{OMe})\text{CH}_2\text{Ph}\}]\text{Cl}$	Under refluxing conditions	56
40.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{R})] + \text{Br}_2$ R same as in 35	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2-$ $\text{C}(\text{C}_6\text{H}_4\text{Br-P})^+\text{Br}_3^-$	-	99
41.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{R})] +$ ArN_2^+ R is same as in 35	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2-$ $\text{C}=\text{C} \begin{array}{c} \text{Ph} \\ \diagup \\ \text{NNAr} \end{array}]^+$	Stirred for 10 minutes	101

..contd.

Table 1 (contd.)

1	2	3	4	5	6
42.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{CR})\text{L}_2] + \text{C}_2(\text{CN})_4$ (R = Ph, Me; $\text{L}_2 = (\text{PPh}_3)_2$, (CO, PPh_3), dppe etc)	Benzene	$[\text{Ru}\{\text{C}[\equiv\text{C}(\text{CN})_2]\text{CPh}=\text{C}(\text{CN})_2\}-$ (L) $(\text{PPh}_3)_3$ (C_5H_5)]	-	98
43.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}\equiv\text{CR})] +$ CHAR=C(CN)X (Ar = $\text{C}_6\text{H}_4\text{NO}_2$ -4; X=CN, CO_2Et)	-	Forms allylic, butadienyl and cyclobutanyl complexes of cyclopentadienyl- ruthenium	-	97
44.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{Ph})] + \text{C}_7\text{H}_7^+ +$ NH_4PF_6	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})-$ $\text{C}=\text{C} \begin{array}{c} \text{Ph} \\ \diagup \\ \text{C}_7\text{H}_7 \end{array}]\text{PF}_6$	-	101
45.	$[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ru}(\text{PPh}_3)_2\text{Cl}] + \text{NaBPh}_4$ (R = H or Me)	Ethylene glycol	$[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ru}(\eta\text{-C}_6\text{H}_5)\text{PPh}_2]-$ BPh_4	-	15
46.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{SnCl}_3] +$ NOX + L (X = Br, NO_2 ; L = Py, $\gamma\text{-pic}$, PPh_3)	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{H}_5\text{-PPh}_2)\text{Ru}(\text{L})\text{NO}_2-$ $\text{SnCl}_3]$	-	108, 109
47.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})] +$ MeI	-	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}=\text{CMePh})]\text{I}$	-	95

..contd.

Table 1 (contd.)

1	2	3	4	5	6
48.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}(\text{PPh}_3)]$ (L = PPh_3 or CO)	NaOMe	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{OR}')(-\text{C}(\text{CH}_2\text{R})(\text{PPh}_3)\text{L})]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{OR}')(-\text{C}(\text{CHR})(\text{PPh}_3)\text{L})]$ (R, R' = Me or Ph)	Deprotonation takes place by NaOMe	54
49.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SP})\text{Cl}] + \text{NaOMe}$ Methanol (SP = $2\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$)		$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SP})\text{H}]$	Refluxed for 1 hour	119
50.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SP})\text{H}] + \text{CS}_2$	-	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCS}_2\{\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_4\text{PPh}_2\}]$	Stirred for 2 days	119
51.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}-\text{C}\equiv\text{C}-\text{CH}_3 - (\text{PMe}_3)_2] + [(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}]$ (M = Cr, Mo, W)	Aceto-nitrile	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CH}_3\text{CN})-(\text{PMe}_3)_2]^+ + \text{Propyne}$	Mixed at 95°C	124
52.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_8\text{H}_{12})\text{Cl}] + \text{NH}_4\text{PF}_6$ (C_8H_{12} = cyclo-octa 1,5 diene)	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_8\text{H}_{10})]^+\text{PF}_6^-$	Refluxed for 3 hours	125
53.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)-\text{CH}(\text{CH}_3)\text{PPh}_2\}\{\text{C}(\text{OCH}_3)-\text{CH}_2\text{C}_6\text{H}_5\}]\text{PF}_6 + \text{LiAlH}_4$	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)-\text{CH}(\text{CH}_3)\text{PPh}_2\}\{\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5\}]$	Treated at -80°C	126

..contd.

Table 1 (contd.)

1	2	3	4	5	6
54.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}] + \text{L}_2$ ($\text{L}_2 = \text{PPh}_2(\text{CH}_2)_2\text{PPh}_2$ etc.)	Heptane	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]\text{Ru}\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}^-$	Stirred for 4 hours	127
55.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCHRCH}_2\text{PPh}_2\}]\text{Ru}\{\text{PPh}_2\text{PCHRCH}_2\text{PPh}_2\}^-$ $\{\text{C}(\text{OCH}_3)\text{CH}_2\text{C}_6\text{H}_5\}[\text{PF}_6 + \text{CH}_3\text{MgBr}]$	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{Ph})\text{PPh}_2\text{PCHRCH}_2\text{PPh}_2]^-$	Mixture kept for 48 hours at room temp.	128
56.	$[(\eta\text{-RC}_5\text{H}_4)\text{RuCl}(\text{PPh}_3)_2] + \text{MS}_2\text{CX}$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CO}; \text{M} = \text{Na, K}$)	Methanol	$[(\eta^5\text{-RC}_5\text{H}_4)\text{Ru}(\text{S}_2\text{CX})(\text{PPh}_3)_2]^-$	-	129
57.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{C-R})\text{L}_2] + \text{X}_2$ ($\text{X} = \text{I, Br, Cl}; \text{R} = \text{Ph, Me}; \text{L}_2 = (\text{PPh}_3)_2, \text{dppe}$)	THF	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{CXR})(\text{PPh}_3)_2]^+$	-	100
58.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru-C}\equiv\text{C-CH}_3(\text{PMe}_3)_2] + \text{HRe}(\text{CO})_5$	CH_3CN	$[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2\text{Ru-CH}_3\text{C}(\text{CO})_2\text{Re}(\text{CO})_8]$	Stirred for 10 minutes at room temp.	130
59.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] + \text{BF}_3\cdot\text{Et}_2\text{O}$ or $\text{HBF}_4\cdot\text{Et}_2\text{O}$	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}\cdot\text{BF}_3]^-$	Adduct formation takes place	131
60.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2] + \text{CS}_2$	C_6H_6	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{S}_2\text{C}\cdot\text{C}_2\text{Ph})]^-$	Refluxed for 4 days	103
61.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{H}] + \text{C}_2(\text{CO}_2\text{Me})_2$ $\text{L}_2 = (\text{PPh}_3)_2$ or dppm	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}]$	Heated for 45 minutes at $82\text{-}86^\circ\text{C}$	132
62.	$[(\eta^5\text{-RC}_5\text{H}_4)\text{RuCl}(\text{PPh}_3)_2] + \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 = \text{tcep}$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CO}$)	Toluene	$[(\eta\text{-RC}_5\text{H}_4)\text{RuCl}(\text{tcep})_2]$	Refluxed for 1.5 hours	133

..contd.

Table 1(contd.)

1	2	3	4	5	6
63.	$[(\eta\text{-CH}_3\text{C}_5\text{H}_4)\text{RuCl}(\text{dppe})] + \text{dtc}$	-	$[\text{Ru}(\text{S}_2\text{CNET}_2)_2(\text{dppe})]$	-	133
64.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2] + \text{dppm} + \text{NH}_4\text{BF}_4$	(i) Toluene (ii) Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppm-P})-(\text{dppm-PP}')]\text{BF}_4$	Refluxed for 16 hours	134
65.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2 + \text{dppf}]$ $\text{dppf} = \text{Fe}(\eta\text{-C}_5\text{H}_4\text{PPh}_2)_2$	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppf})\text{Cl}]$	Refluxed for 16 hours	135
66.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\text{dppf}) + \text{dimethyl acetylene-dicarboxylate}]$	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{dppf})]$	Refluxed for 4 hours	135
67.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{R})\text{CH}(\text{R}')-\text{PPh}_2\}\{\text{C}=\text{CH}(\text{Bu})\}]\text{PF}_6 + \text{CH}_2\text{N}_2$ (R, R' = Me)	THF/ Ether	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{R})-\text{CH}(\text{R}')\text{PPh}_2\}(\text{L})]\text{PF}_6$	Treated for 16 hours at room temp.	136
68.	$[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}]_4 + \text{PR}_3$ R = Pr or Cy (cyclohexyl)	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)\text{Cl}]$	Reac. at room temp.	137
69.	$[(\eta^5\text{-C}_5\text{Me}_5)\text{RuX}]_n + \text{L}$ (L = 1,5-cyclooctadiene, 2,2'-bipyridine; X=Cl or OMe)	-	$[(\eta^5\text{-C}_5\text{Me}_5)\text{RuX}(\text{L})]$	-	138
70.	$[(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)] + \text{HBF}_4 \cdot \text{Et}_2\text{O}$	Toluene	$[(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_2(\text{PPh}_3)_2]\text{BF}_4$	Reaction takes place at -78°C	139
71.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2 + \text{AsPh}_3]$	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{AsPh}_3)(\text{PPh}_3)]$	Refluxed for 24 hours	140

..contd.

Table 1 (contd.)

1	2	3	4	5	6
72.	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\text{AsPh}_3)_2(\text{PPh}_3)] + \text{R}$ (R = KX, HX, SnCl ₂ ; X = F, Br, I, CN)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2(\text{PPh}_3)_2\text{X}]$	-	140
73.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2(\text{PPh}_3)\text{Cl}] +$ $\text{X}^- = \text{BPh}_4^-, \text{HgCl}_3^- \text{ or } \text{Zn}_2\text{Cl}_6^{2-}$	Acetonitrile	$[(\eta^5\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2(\text{PPh}_3)_2(\text{MeCN})]^+\text{X}^-$	Refluxed for about 20 minutes	140
74.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}] \cdot 3/4 \text{ CH}_2\text{Cl}_2$ + 2,2'-Bipyridyl	Methanol	$[\text{RuCl}_2(\text{AsPh}_3)_2(\text{bipy})]$ and $[\text{Ru}_2\text{Cl}_4(\text{bipy})_3(\text{AsPh}_3)_2]$	Refluxed in nitrogen purged solution for 3-4 hours	141
75.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}] \cdot 3/4 \text{ CH}_2\text{Cl}_2$ + 1,10-O-phenanthroline	Methanol	$[\text{RuCl}_4^{2-}(\text{o-phen})_3]$ and $[\text{Ru}_2\text{Cl}_4(\text{AsPh}_3)_2(\text{o-phen})_2] \cdot \text{CH}_2\text{Cl}_2$	Same as in 74	141
76.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}] + \text{SbPh}_3$	Benzene	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$	Refluxed for 30 hours	142
77.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{H}] + \text{KX}$ (X = F ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NCS ⁻)	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{X}]$	Refluxed for some time	142
78.	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}] + \text{Y}^-$ (Y ⁻ = BPh ₄ ⁻ , HgCl ₃ ⁻ , Zn ₂ Cl ₆ ²⁻)	Acetonitrile	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Y}]^+\text{Y}^-$	Refluxed for a brief period	142
79. (a)	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPH}_3)_2\text{X}] + \text{L}$ (L = Py or 7-pic; E = As or Sb; X = Cl, Br, I, CN, NCS etc.)	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPH}_3)_2\text{LX}]$	-	143

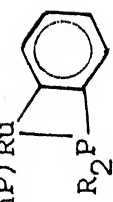
..contd.

Table 1(contd.)

1	2	3	4	5	6
(b)	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{X}](\text{E}=\text{P or Sb})$ + L-L (L-L = DTC or acac X = same as in (a))	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{L-L}]^+\text{X}^-$	Refluxed for several hours	
(c)	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{X}](\text{E}=\text{P, As or Sb})$ + L-L + Y ⁻ L-L = 2,2'-bipyridine or 1,10-phenanthroline Y ⁻ = BF ₄ ⁻ , BPh ₄ ⁻ , ClO ₄ ⁻ , HgCl ₄ ⁻ etc	Ethanol	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{L-L}]^+\text{Y}^-$		
80.	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{Cl})\text{L}_2] + [\eta^5\text{-C}_5\text{H}_5\text{-RuL}_2(\text{CN})]$ L = PPh ₃ , AsPh ₃ , SbPh ₃ + NaBF ₄	Methanol	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{Ru-CN-Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2]^+\text{BF}_4^-$ (E = P, As or Sb)	Stirred at 50°C for 1-2 hours	144
81. (a)	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2\text{X}] + \text{NOX}$ (E = P, As, Sb; X = Cl, Br, I, CN etc.)	Methanol and CH ₂ Cl ₂	$[\text{Ru}(\text{NO})\text{X}_3(\text{EPh}_3)_2]$	Refluxed for an hour	145
(b)	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\text{EPh}_3)_2(\text{L-L})\text{X}] + \text{NOBr}_3$ (E = As, Sb; L-L = 2,2'- bipy; 1,10-phen)	MeOH: CH ₂ Cl ₂ 2:1	$[\text{Ru}(\text{Br}_3)(\text{EPh}_3)_2\text{L-L}]$	Refluxed for an hour	
82. (a)	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{RuSnCl}_3(\text{PPh}_3)_2] + \text{NOX}$ (X = Cl, Br, Br ₃)		$[\text{Ru}(\text{NO}_2)\text{SnCl}_3(\text{PPh}_3)_2\text{-}(\pi\text{-C}_6\text{H}_5\text{-PPh}_2)]$		146

..contd.

Table 1 (contd.)

1	2	3	4	5	6
(b)	$[(\eta^5\text{-C}_5\text{H}_5)\text{RuSnCl}_3(\text{EPh}_3)_2] +$ NOX + Excess EPh_3 (X = Cl, Br; E = As, Sb)		$[\text{Ru}(\text{NO})\text{X}_3(\text{EPh}_3)_2]$ + $[\text{Ru}(\text{NO}_2)\text{SnCl}_3(\text{SbPh}_3)(\pi\text{-C}_6\text{H}_5)\text{-SbPh}_2]$		
83.	$[\text{CP}^*\text{RuCl}_2]_2$ or $[\text{CP}^*\text{RuCl}_2(\text{Pyr})]$ + NaOMe ($\text{CP}^* = \eta^5\text{-C}_5\text{Me}_5$)	Methanol	$[\text{CP}^*\text{Ru}(\text{OMe})]_2$	Stirring 36 h at room temp.	147
84.	$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2\text{Cl} + \text{NOCl}]$	CH_2Cl_2	$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NO})\text{Cl}_2]$	Stirring for 46 h at room temperature	148
85.	$\text{CP}(\text{R}_2\text{PhP})_2\text{RuCl} + \text{H}_3\text{CM}$ $\text{CP} = \text{C}_5\text{H}_5; \text{C}_5\text{Me}_5$ $\text{R} = \text{Me}, \text{Ph}$ $\text{M} = \text{Li}, \text{MgCl}$	Toluene	$\text{CP}(\text{R}_2\text{PhP})_2\text{RuMe}$ $\xrightarrow{-\text{CH}_4}$ $\text{CP}(\text{R}_2\text{PhP})\text{Ru}$ 	Heating for 24h at 100- 140°C	149

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CHAPTER II

INSERTION REACTIONS OF CARBONYL SULFIDE AND CARBON-DISULFIDE WITH $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) AND $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppm)

Introduction

Despite the extensive literature on the insertion reactions of small molecules the number of reports on the reactivity of heteroallenes (CXY) ($\text{X}, \text{Y} = \text{O}, \text{S}, \text{Se}$) towards M-H or M-alkyl bonds and especially towards complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{X}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ (I) ($\text{X} = \text{H}, \text{alkyl}, \text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) or $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L-L})\text{X}]$ ($\text{L-L} = \text{dppe}$ or dppm) remains small. Though recently some papers concerning the formation of dithioformates or formates as a result of transition metal hydride reactions with CS_2 or CO_2 respectively have appeared,¹⁻¹⁰ COS reactions with metal hydrides yielding monothioformates are almost missing, when one would expect a parallel behaviour of COS with CO_2 or CS_2 because of its similarity with them. Previous work indicate only one or two such examples.^{4,11} In addition, COS, being susceptible to easy decomposition into CO and S, may also provide a convenient route for metal carbonyl synthesis under ambient conditions.¹²

Considering these, the paucity of COS insertion reactions and the versatility of the reactivity of (I),¹³⁻¹⁸ we became interested in COS reactions with the latter complexes. This chapter reports the results of such a study. Furthermore, since a reaction of CS₂ with [Ru(η^5 -C₅H₅)H(PPh₃)₂] has already appeared in the literature,¹⁹ we also wish to describe herein similar reactions of CS₂ with [Ru(η^5 -C₅H₅)H(EPh₃)(E'Ph₃)] (E, E' = As, Sb) as an extension to the previous work.

Experimental

All the chemicals used were of Analar grade. Solvents were dried before use. The complexes and dry COS gas were prepared by the literature methods.^{17,18,20} CS₂ was distilled from P₂O₅ prior to use.

The analytical and spectral data of the products were obtained as described elsewhere.¹⁸ Molecular weights were taken on Kanuer Vapour Pressure Osmometer. The ¹³C n.m.r. spectra of the compounds were taken on JEOL FT-90 spectrophotometer. The results are given in Table II.1.

(A) Reactions of COS with [Ru(η^5 -C₅H₅)H(EPh₃)(E'Ph₃)] (E, E' = P, As, Sb)

In a typical experiment, gaseous COS was allowed to pass through a 30 ml stirred methanolic suspension (ca. 0.004 M in

hydride) for about 2 h whereby the suspension changed into a greenish brown solution. It was centrifuged. Removal of the solvent from the centrifugate under low pressure yielded a greenish yellow coloured complex which was crystallised from CH_2Cl_2 /Petroleum ether. The acetone (dried) solution of the crystallized product was allowed to run down a freshly prepared neutral alumina column and eluted with acetone. The eluent was concentrated under low pressure yielding pure microcrystalline product. It was vacuum dried and analyzed. A few PPh_3 containing products decomposed on the alumina column and therefore the solutions of these compounds were not passed through the column. They were analyzed as such.

(B) Reactions of CS_2 with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E} = \text{Sb}$, $\text{E}' = \text{P, As, Sb}$) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppm)

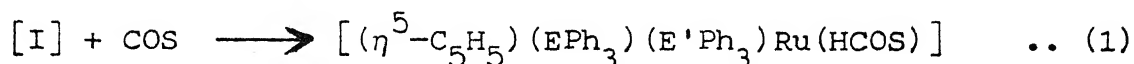
Stirring a 30 ml CS_2 solution of the hydride (ca. 0.004 M) for about 8 h at room temperature yielded a dark red solution which was worked out by the same procedure as in (A) to give red brown microcrystalline product. All the complexes were purified by neutral alumina column chromatography.

(C) Reactions of COS with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppm)

The procedure followed was similar to that in (a) except that COS gas was passed in the methanolic suspension for a longer time here (4-6 h).

Results and Discussion

Reactions of COS with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) or $[(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppm) (partially soluble) in CH_3OH produce greenish yellow microcrystalline complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)(\text{HCOS})]$ or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})(\text{HCOS})]$ eq. 1.



which were purified by recrystallization from CH_2Cl_2 /petroleum ether followed by column chromatography. The products were characterized by elemental analyses, molecular weights and spectroscopy. The presence of coordinated COS in the form of monothioformate is confirmed by the i.r. spectra in which the characteristic bands arising due to $\nu(\text{C}=\text{S})$ and $\nu(\text{CO})$ of the coordinated $(\text{HCOS})^-$ besides those of the coordinated $(\eta^5\text{-C}_5\text{H}_5)$ and $(\text{EPh}_3, \text{E}'\text{Ph}_3, \text{dppe}$ or $\text{dppm})$ are observed at 1100 cm^{-1} and 1661 cm^{-1} respectively (Fig. II.1). Room temperature ^1H n.m.r. spectra of all the COS reaction complexes (recorded in CDCl_3) are similar (Fig. II.2 and II.3). These spectra support the presence of C_5H_5 ring bonded as $\eta^5\text{-C}_5\text{H}_5$ ($\delta + 4.59$, singlet, integrating for 5H) and the hydrogen atom as H-C ($\delta = 11.48$ ppm, singlet, integrating for 1H). They also exhibit multiplets associated with $\text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm protons (ca. $\delta + 7-8$ ppm). In the ^{13}C n.m.r. spectrum, the thiocarbonyl carbon resonates at

δ 181.87 ppm, $\eta^5\text{-C}_5\text{H}_5$ carbons resonate at δ 82.6 ppm and the phenyl carbons as multiplets in the regions δ 127.9–137.4 ppm.

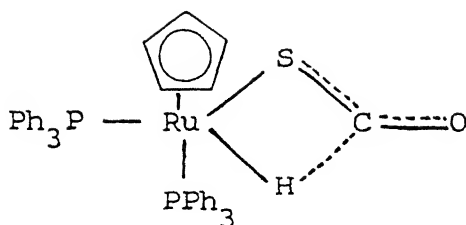
These complexes are highly soluble in halogen containing and polar organic solvents, but insoluble or less soluble in hydrogen type solvents.

The reddish brown coloured solids obtained by the reactions of CS_2 with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppm) are formulated as $[\text{Ru}(\text{SCHS})(\eta^5\text{-C}_5\text{H}_5)(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ or $[\text{Ru}(\text{SCHS})(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})]$ on the basis of elemental analysis, spectroscopy and molecular weights. Their i.r. spectra exhibit, besides the characteristic bands of cyclopentadiene and E (or E') Ph_3 , dppe or dppm an intense broad band around 1000 cm^{-1} with a shoulder of medium intensity around 970 cm^{-1} . These have been assigned to $\nu_{\text{asy}}(\text{C}=\text{S})$ and $\nu_{\text{sym}}(\text{C}=\text{S})$ respectively confirming to the earlier data of dithioformate complex.¹⁹ Their room temperature ^1H n.m.r. spectra (CDCl_3) feature absorbances similar to those observed in the spectra of COS reaction products. In the ^{13}C n.m.r. spectrum, the thiocarbonyl carbon resonates at δ 175.6 ppm, $\eta^5\text{-C}_5\text{H}_5$ carbons resonate at δ 83.2 as singlet and phenyl carbons in the region δ 127.9–137.4 as multiplets. These data imply that the complex contain dithioformate as one of the coordinated ligands. The CS_2 reaction complexes are relatively more stable compared to those of COS reactions which means they can also be further purified chromatographically. (Presumably the stability of these complexes correlates

with the basicity of dithio and monothioformates). Their solubilities in various solvents are similar to those of the COS reaction products.

The implication of the preceeding results is that the structures of these complexes could be explained in terms of (a) bidentacy or (b) monodentacy of di and mono-thioformates towards one metal ion. Although the spectral data could not unambiguously distinguish between the two alternatives, the interaction of these ligands with the metal ion as bidentate would yield an unlikely twenty electron system with an increased coordination number (five or seven depending upon the Cp behaving as mono or tridentate respectively). Taking into account the unstability of a twenty electron system, the monodentacy of these ligands has been assumed in our complexes. Furthermore, the monodentacy of monothioformates requires a choice to be made between sulfur and oxygen as the bonding site. In the absence of X-ray data, the preferential soft sulfur-soft ruthenium (II) interaction is rationalized on the basis of HSAB principle.

In general, the mechanism of insertion reactions of COS or CS₂ into metal hydrogen bonds should presumably be akin to that of other analogous insertion processes,⁷ in which the reaction occurs via adduct formation, followed by rapid metal-hydrogen bond cleavage with concomitant C-H bond formation.



The present system being coordinatively saturated, formation of a four centred transition state⁷ for COS or CS₂ insertion should proceed with initially loss of one of EPh₃ molecule, though a possibility of thermodynamically relatively unstable activated complex without prior loss of an EPh₃ molecule with the formation of a five coordinated 20 electron system and a concomitant coordination of COS or CS₂ at the metal centre also exists. The lack of kinetic data does not allow us to make a choice between the two alternatives. However in both the cases an acid-base interaction of the anionic hydride at the electrophillic carbon centre may occur prior to the formation of a four centred transition state, followed by finally formation of di- or monothioformato complexes. An interaction of this type has been observed in a number of cases cited in the literature.

Table II.1. Analytical and spectral data of the complexes

Sl. No.	Name of the Complex (m.p., colour)	Analyses Found %			I.R. data (cm ⁻¹)		NMR data		Molecular weight Found[Calcd]
		C	H	S			¹ H NMR δ(ppm)	¹³ C NMR δ(ppm)	
1	2	3			4		5		6
1.	[Ru(OCHS)(PPh ₃) ₂ (η ⁵ -C ₅ H ₅)](145° GY)	66.7 (67.1)	4.4 (4.8)	5.0 (4.26)	1661(s)ν(C=O) 1095(s)ν(C=S)		11.48(CHS)	181.8, t, (CHS)	736 (751)
2.	[Ru(OCHS)(AsPh ₃) ₂ (η ⁵ -C ₅ H ₅)](127-130° YB)	62.2 (60.9)	4.6 (4.3)	4.2 (3.8)	1660(s)ν(C=O) 1100(s)ν(C=S)		11.5 (CHS)	181.64, t, (CHS)	825 (839)
3.	[Ru(OCHS)(SbPh ₃) ₂ (η ⁵ -C ₅ H ₅)](130° YB)	54.0 (53.1)	3.9 (4.37)	3.4 (4.5)	1658(s)ν(C=O) 1094(s)ν(C=S)		11.5 (CHS)	179.9, t, (CHS)	918 (933)
4.	[Ru(OCHS)(AsPh ₃)(PPh ₃)(η ⁵ -C ₅ H ₅)](133-135° YB)	63.4 (64.05)	4.5 (4.8)	4.0 (3.5)	1665(s)ν(C=O) 1100(s)ν(C=S)		11.48(CHS)	180.8, t, (CHS)	800 (795)
5.	[Ru(OCHS)(PPh ₃)(SbPh ₃)(η ⁵ -C ₅ H ₅)](128° YB)	59.8 (58.9)	4.27 (4.5)	3.8 (4.4)	1660(s)ν(C=O) 1095(s)ν(C=S)		11.54(CHS)	181.8, t, (CHS)	830 (842)
6.	[Ru(SCHS)(AsPh ₃) ₂ (η ⁵ -C ₅ H ₅)](115-120° RB)	58.9 (59.5)	4.2 (5.1)	7.4 (8.1)	1020(br)ν(C=S)		11.6(CHS)	175.6, t, (CHS)	831 (855)
7.	[Ru(SCHS)(SbPh ₃) ₂ (η ⁵ -C ₅ H ₅)](100-105° RB)	53.0 (54.1)	3.8 (4.9)	6.7 (7.2)	985m(br)ν(C=S)		11.58(CHS)	175.8, t, (CHS)	932 (949)
8.	[Ru(SCHS)(AsPh ₃)(PPh ₃)(η ⁵ -C ₅ H ₅)](110-115° RB)	62.1 (62.84)	4.4 (3.7)	7.9 (8.3)	1020(s)ν(C=S)		11.6(CHS)	176.2, t, (CHS)	792 (811)
9.	[Ru(SCHS)(PPh ₃)(SbPh ₃)(η ⁵ -C ₅ H ₅)](115-120° RB)	58.9 (60.13)	4.2 (5.05)	7.5 (7.9)	990m(br)ν(C=S)		11.6(CHS)	176.0, t, (CHS)	843 (858)
10.	[Ru(OCHS)(dppe)(η ⁵ -C ₅ H ₅)](155° YB)	62.0 (61.4)	5.3 (4.8)	4.8 (5.1)	1615(br)ν(C=O) 1100(s)ν(C=S)		10.9(CHS)	176.9(CHS)	610 (625)

...contd.

Table II.1(contd.)

1	2	3	4	5	6			
11.	[Ru(OCHS) (dppm) ($\eta^5\text{-C}_5\text{H}_5$)] (148° YB)	60.2 (60.8)	4.9 (4.6)	5.0 (5.2)	1610(br) ν (C=O) 1095(s) ν (C=S)	11.0(CHS)	177.0(CHS)	598 (611)
12.	[Ru(SCHS) (dppe) ($\eta^5\text{-C}_5\text{H}_5$)] (130° RB)	60.5 (59.9)	5.0 (4.7)	9.1 (9.9)	1000(br) ν (C=S)	10.7(CHS)	177.4(CHS)	615 (641)
13.	[Ru(SCHS) (dppm) ($\eta^5\text{-C}_5\text{H}_5$)] (125° RB)	60.0 (59.3)	4.9 (4.4)	10.8 (10.2)	1010(br) ν (C=S)	10.6(CHS)	177.5(CHS)	595 (627)

GY = Greenish yellow; YB = Yellowish brown; RB = Reddish brown; (CHS) = Thioformato group.

DPPE = 1,2 Bis(diphenylphosphinoethane); DPPM = 1,2 Bis(diphenylphosphinomethane).

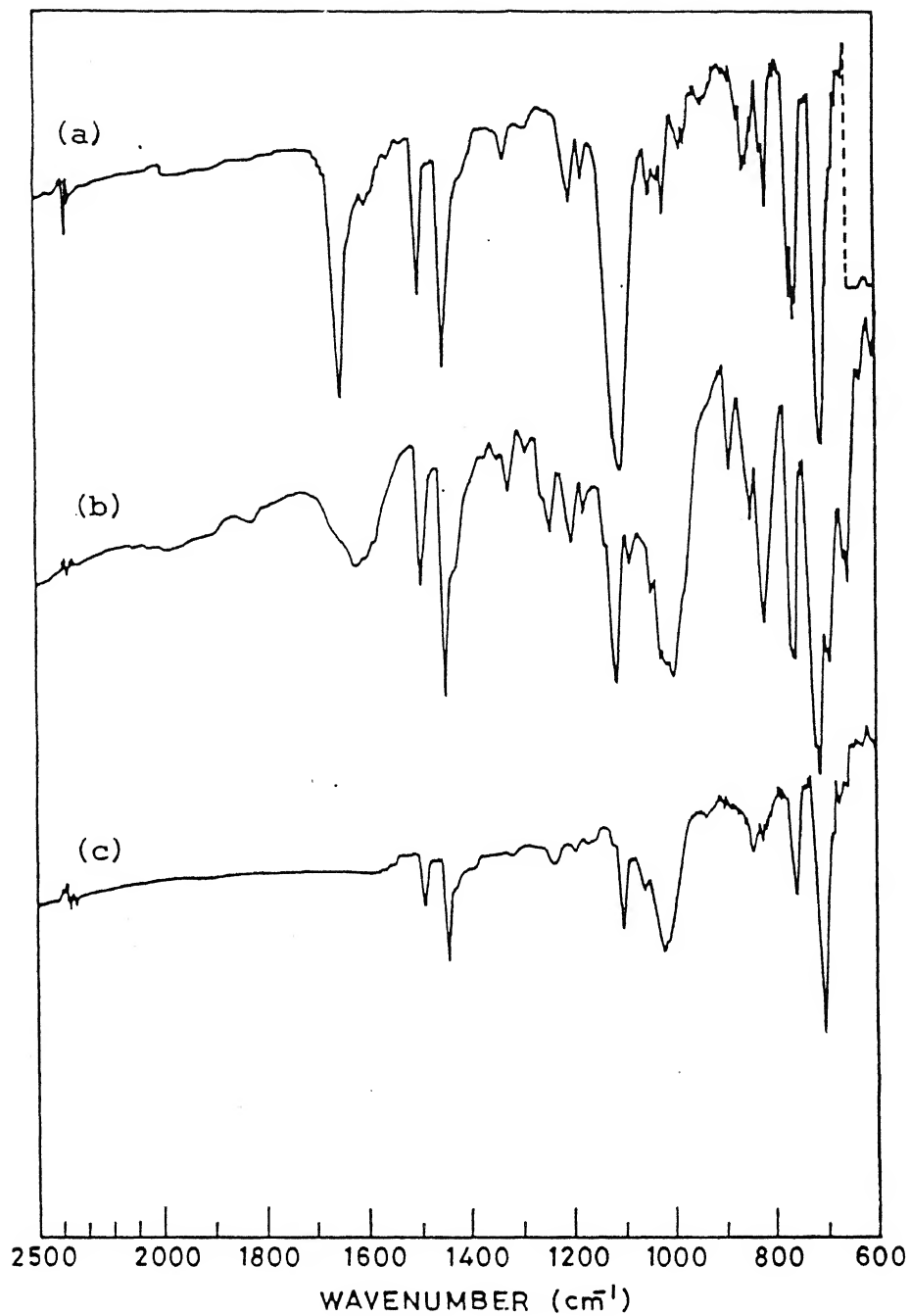


Fig. II.1. Infra Red Spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{HCOS})]$,
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})(\text{HCOS})]$ and (c) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2(\text{HCS}_2)]$

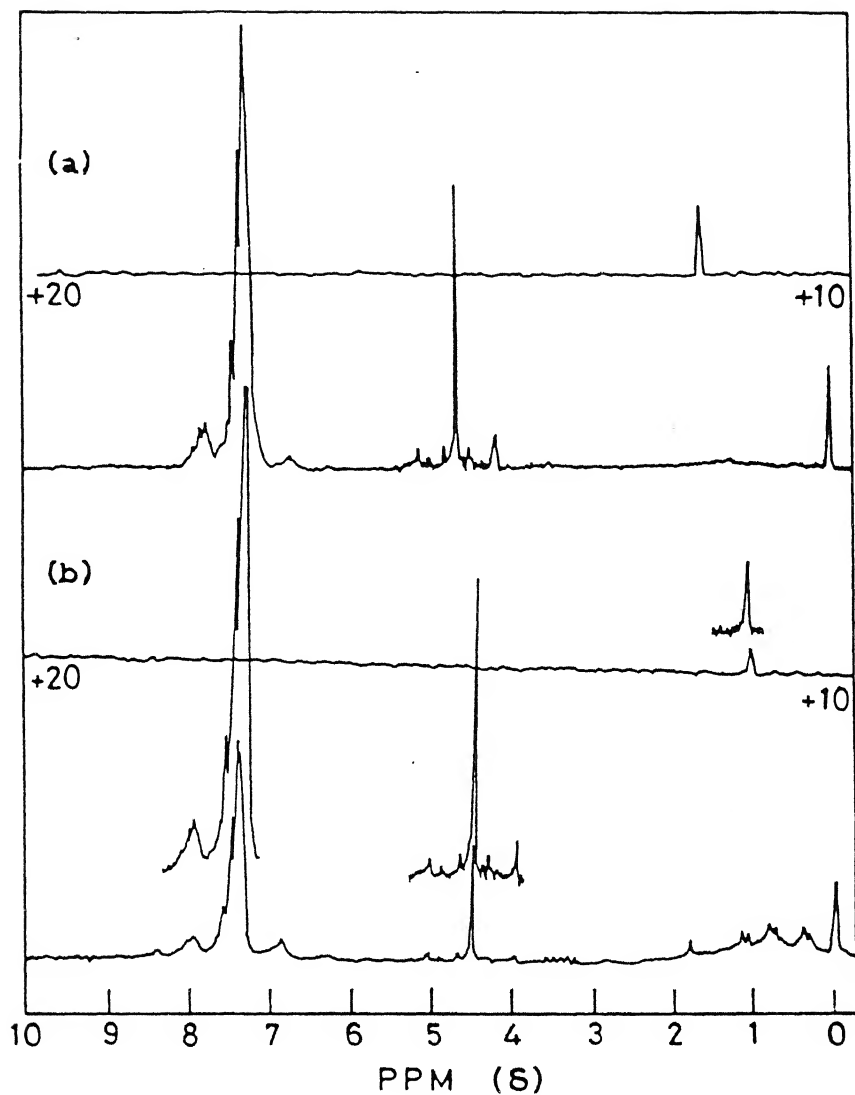


Fig.II.2. ^1H NMR spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{-(HCOS)}]^-$ and (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{-(HCS}_2)]^-$

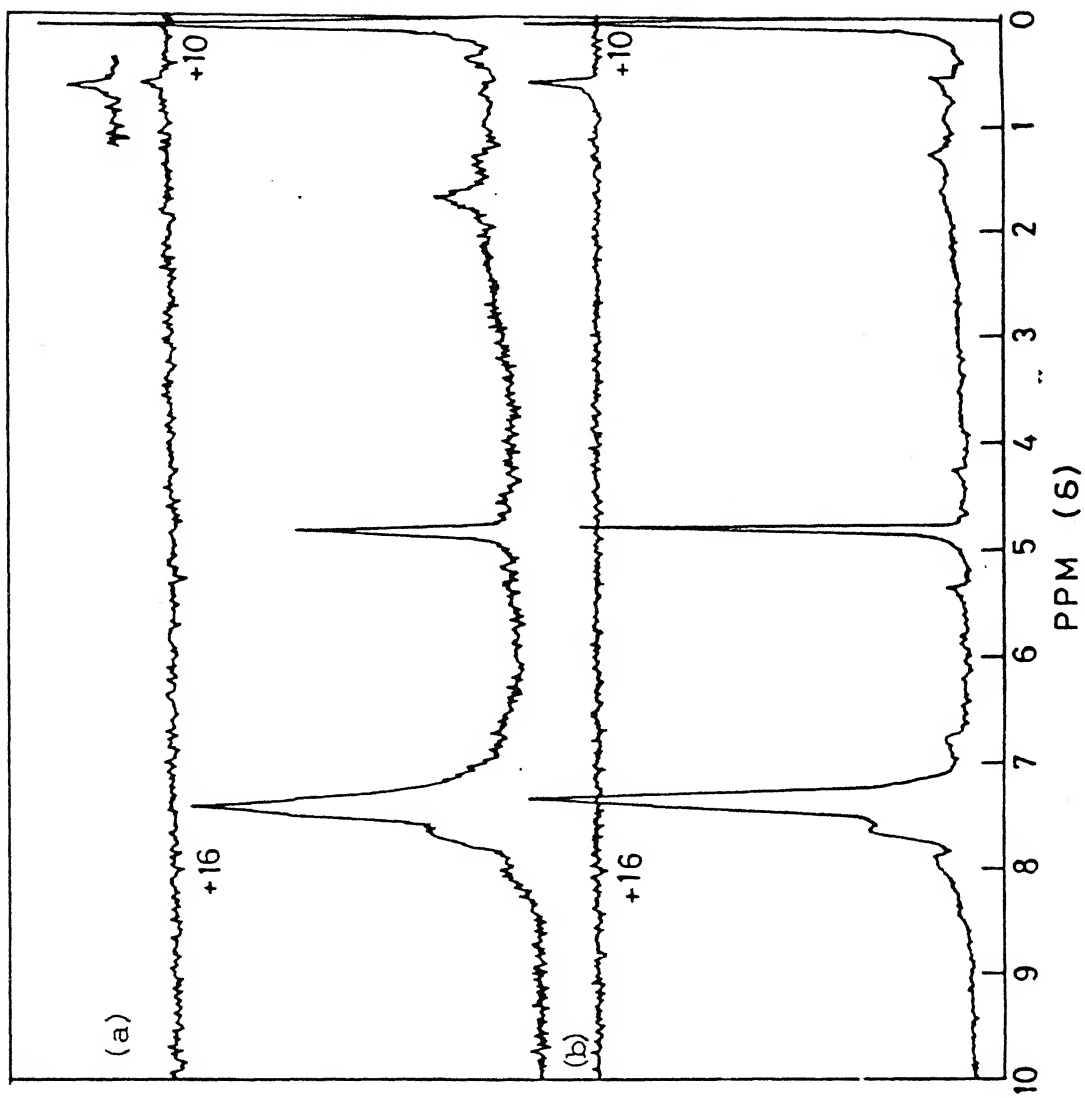


Fig.II.3. ^1H NMR Spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})(\text{HCS}_2)]$ and
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})(\text{HCOs})]$

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Chapter III

Part I: REACTIONS OF 1-ETHYNYL PYRENE WITH CYCLO-PENTADIENYL RUTHENIUM COMPLEXES

Introduction

Many papers¹⁻⁵ have appeared describing the reactions between alk-1-yne, (HC_2R) and the complexes $[RuR'L_2(\eta^5-C_5H_5)]$ ($R'=Cl^-$, H^- , Me^- or CH_2Ph^- ; L_1 = trivalent P, As or Sb derivatives, L_2 = trivalent P, As, Sb derivatives, CO and other related ligands; L_1, L_2 = dppe or dppm). These reactions have given a variety of unusual products, containing η' -vinylidene or η' -ethynyl derivatives which in turn react with methanol and higher alcohols to give cations $[RuL_1L_2(\eta^5-C_5H_5)\{C(OR)CH_2R\}]^+$ and other interesting products.^{4,5} The reactivity of these reactions is influenced by the subtle changes (steric or/and electronic) within the coordination sphere of the metal. This is evident from the different stoichiometries of the products obtained from the reactions of $[RuL_1L_2(\eta^5-C_5H_5)(C_2HR)]^+$ or $[RuL_1L_2(\eta^5-C_5H_5)(C_2R)]$ and methanol or alcohols. Literature survey indicates practically very little work showing the effect of the alkyne substituents on the reaction rates. In continuation with our earlier work in this area we describe in this chapter (Part I) the synthesis and characterization

of products obtained from the reactions of 1-ethynyl pyrene $[\text{HC}_2(\text{pyrene})]$ with the complexes $[\text{RuL}_1\text{L}_2\text{Cl}(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}, \text{dppm}$). The cationic and the neutral products obtained from these reactions were further treated with methanol and higher alcohols and characterized resulting products have also been described herein.

Experimental

All the chemicals of chemically pure grade were used without further purification. Solvents were dried before using them.⁶ The complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_1\text{L}_2\text{Cl}]$ ($\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm) were prepared by the literature methods.⁷⁻¹⁰ The analytical and the spectral data of the products were obtained as described elsewhere.⁸ The ^{13}C n.m.r. spectra of the complexes were taken on Jeol-FT-90 Spectrophotometer.

(a) Preparation of Vinylidene Complexes from 1-Ethynyl Pyrene

Preparation of $[\text{Ru}(\text{C=CHR})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$ ($\text{R}=\text{Pyrene}$);

($\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm)

Addition of NH_4PF_6 (65 mg, 0.39 mmol) and 1-ethynyl pyrene (40 mg, 0.18 mmol) to a suspension of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_1\text{L}_2\text{Cl}]$ ($\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm) (100 mg, 0.13 mmol) in methanol (20 ml), followed by heating for a brief period of about half an hour under reflux, gave a deep red solution which

was filtered and evaporated. The red coloured crystals were separated which were extracted with dichloromethane (5 ml). Excess diethyl ether was added to the dichloromethane extract whereby a reddish tan precipitate of $[\text{Ru}(\text{C}=\text{CHR})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$ was separated. It was centrifuged out, washed several times with ether and dried in vacuum (yield, ca. 40%). The tetrafluoroborate or tetraphenylborate salts of the complexes were obtained by the procedure similar to (a) except that about 50 mg of NaBF_4 or NaBPh_4 was added in place of NH_4PF_6 (yield, ca. 35%).

(b) Preparation of η' -Alkynyl Derivatives: Preparation of complexes $[\text{Ru}(\text{C}_2\text{R})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]$ (R=pyrene, $\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm)

A solution of $[\text{Ru}(\text{C}=\text{CHR})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$ (R=pyrene, $\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm) in CH_2Cl_2 (5 ml) was transferred to a short column of chromatographic alumina on adsorption, the red colour of the cation was discharged, and elution with ether gave a yellow fraction. Evaporation and recrystallization ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) afforded yellow microcrystalline product of $[\text{Ru}(\text{C}_2\text{R})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]$ (R = pyrene, $\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}, \text{dppm}$). It was centrifuged out, washed with methanol and dried in vacuo (yield, ca. 30%).

(c) A mixture of $[\text{RuClL}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm) (100 mg, 0.13 mmol) and 1-ethynyl pyrene (40 mg, 0.18 mmol) was heated in refluxing methanol (20 ml) for about 30 minutes. Sodium methoxide (1 ml of a 1M solution in methanol) was added to the deep red solution and the yellow crystals that rapidly deposited were recrystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give pure compound which was found to be identical with the product obtained by method (b).

(d) Attempts to prepare $[\text{Ru}\{\text{C}(\text{OMe})\text{CH}_2\text{R}\}(\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5))](\text{PF}_6, \text{BF}_4 \text{ or } \text{BPh}_4)$

Addition of $\text{HPF}_6, \text{OEt}_2$ (0.5 ml) to a suspension of $[\text{Ru}(\text{C}_2\text{R})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ (100 mg, 0.13 mmol) in methanol (20 ml) gave a red solution of the vinylidene complex. The solution was refluxed for 24 hrs. No change in the colour of the solution was observed. The solution was cooled to room temperature, filtered and concentrated to dryness. The residue was extracted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$. The red compound thus obtained was analyzed for $[\text{Ru}(\text{C}=\text{CHR})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$. In these reactions we were not able to obtain the expected methoxy (pyrene) carbene complex $[\text{Ru}\{\text{C}(\text{OMe})\text{CH}_2\text{R}\}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$. The reactions described in (d) above were further repeated except that the time of reflux for the deep red solution was increased from 24 hours to 48 hours. The products obtained in these reactions were found to be identical to those obtained in (d).

Results and Discussion

The analytical data of the complexes suggest that mono-substituted vinylidene complexes of ruthenium could be prepared in high yields by the reactions of pyrene substituted alk-1-yne and chlororuthenium precursors in presence of a large anion like PF_6^- . These dark red crystalline salts $[\text{Ru}(\text{HC}_2\text{R})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]\text{-PF}_6^-$ (R = pyrene, L_1, L_2 = PPh_3 , AsPh_3 , SbPh_3 , dppe or dppm) were found to be soluble in dichloromethane, acetone, tetrahydrofuran; moderately soluble in benzene, methanol but insoluble in light-petroleum and diethyl ether. Their infra red spectra did not exhibit any band in the region $2100\text{--}1700\text{ cm}^{-1}$ indicating the absence of $\nu\text{C}\equiv\text{C}$ in the complex. One extra band of medium intensity, not present in the spectrum of 1-ethynyl pyrene, was however found at 1640 cm^{-1} . The latter band has been assigned to the characteristic vibration of vinylidene moiety $\nu(\text{C}=\text{C})^5$ (Table III.1). Strong absorptions at 840 cm^{-1} (or 1050 cm^{-1}) are characteristic of PF_6^- or BF_4^- anion.⁵

The presence of $(\text{-C}=\text{CH-R})$ group has also been confirmed by their ^1H n.m.r. spectra. These exhibited the expected sharp singlet at δ 4.5 assigned to C_5H_5 protons, and broad multiplets in the aromatic region (δ 7.1-7.8) and δ (8.0-8.8) assigned to the protons of the ligand L_1, L_2 and those of pyrene ring respectively. In addition they also contained a triplet at δ 5.4, assigned to a single proton of the moiety $\text{-C}=\text{CHR}$, coupled to two

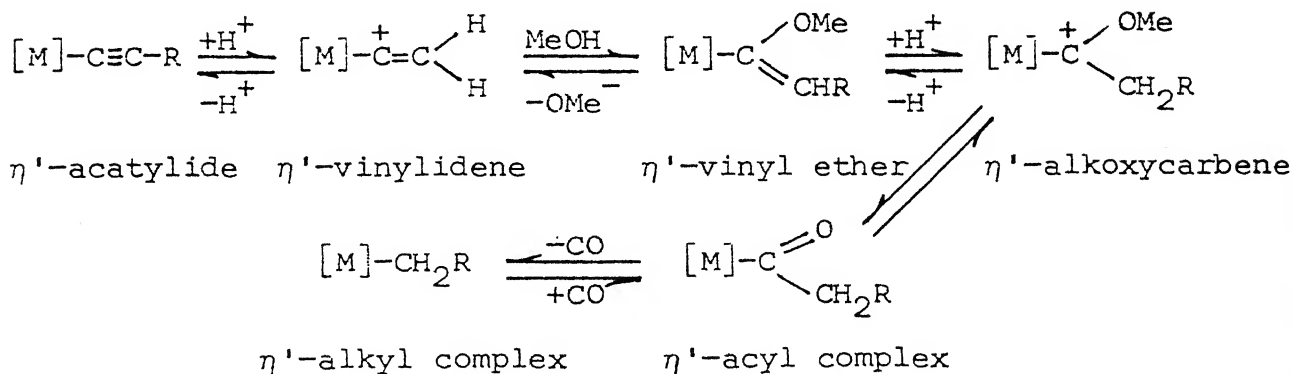
phosphorus nuclei⁵ or PPh_3 , dppe or dppm containing complexes. In case of As or Sb complexes the splitting of the band is not observed.

Their ^{13}C n.m.r. spectra exhibited a band around δ 125 besides the usual ones due to the carbon of $\eta^5\text{-C}_5\text{H}_5$ (ca. δ 85.6) and phenyl groups (ca. δ 127.4-134). The band around δ 125 has been assigned to C^{II} of $\overset{\text{I}}{\text{C}}=\overset{\text{II}}{\text{CHR}}$ which further supports the presence of vinylidene group.⁵ Vinylidene complexes were readily deprotonated on treatment with a base. Elution with diethyl ether afforded a bright yellow fraction, which was shown to contain the neutral ethynyl pyrene complex $[\text{Ru}(\text{C}_2\text{R})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]$. The same compounds were also obtained by the addition of sodium methoxide to the cationic complex formed, in situ. In the latter method conversion was almost quantitative. Vinylidene complexes were also deprotonated with formation of the neutral complexes on treatment with sodium borohydride or lithium aluminium hydride. These complexes have been characterized by the presence of a medium intensity $\nu(\text{C}\equiv\text{C})$ band at about 2000 cm^{-1} in their infrared spectra (Table III.1). The disappearance of the band due to $-\text{C}=\text{CHR}$ proton at δ 5.4 in the n.m.r. spectra also confirmed the formation of the neutral η^1 -ethynyl complexes. ^1H n.m.r. spectra also showed bands at δ 4.5, $\eta^5\text{-C}_5\text{H}_5$ protons (Table III.1); δ (7.2-7.8) phenyl protons and δ (8.0-8.8) pyrene ring protons. The complexes were highly soluble in CH_2Cl_2 , slightly soluble in chloroform, CCl_4 and insoluble in petroleum ether and diethyl

ether. Because of the low solubility in chloroform the ^1H n.m.r. spectra for the cationic vinylidene complexes could not be taken in CDCl_3 .

The relative stability of the cationic vinylidene complexes could be explained by the delocalization of positive charge on the metal ion over the pyrene ring attached to the alkyne carbon, which in turn, gets stabilized by the delocalized π -electron cloud over the pyrene ring. The stability of these cationic complexes suggest that the neutral η' -ethynyl derivatives might get protonated to reform the cations. Addition of HBF_4 or HPF_6 to a solution of $[\text{Ru}(\text{C}_2\text{R})\text{L}_1\text{L}_2(\eta^5\text{-C}_5\text{H}_5)]$ (R = pyrene, $\text{L}_1, \text{L}_2 = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{dppe}$ or dppm) in dichloromethane resulted in an immediate change in colour from yellow to deep red. Addition of diethyl ether resulted in precipitation of a salt which was identical in all respects to the vinylidene complex. This deprotonation-protonation cycle could be repeated many times with out apparent loss of complex.

It has been demonstrated that η' -acetylide complexes can be linked with the η' -alkyl complexes⁴ (Scheme III.1).



Scheme III.1

The reactions in Scheme 1 are influenced by both steric and electronic factors arising out of the substituents on alk-1-yne and the ligands in the coordination sphere of the metal ion. Since the vinylidene complexes synthesized by us contains a planar pyrene ring attached to $-C=CH$ group, it is difficult to predict the extent to which the pyrene ring exhibit steric effect. Therefore reactions of η' -acetylide complexes with alcohols in presence of acids were carried out. In all the cases we were unable to obtain any cationic η' -vinyl ether complexes from the reactions of alcohols with either $[M]-C\equiv C-R$ in presence of $HPF_6 \cdot Et_2O$ or η' -vinylidene complexes. In every case η' -vinylidene complex has been separated out. We suggest that steric congestion about the ruthenium in the $Ru(\eta^5-C_5H_5)L_1L_2$ moiety along with the large pyrene group substituted in acetylide group apparently prevents access of the bulky nucleophile OMe^- or OR^- to the α -carbon of acetylene or vinylidene. Though the electronic influence of the pyrene group may also play a part in making the attack of OR^- group more difficult, but the influence of electric factors at this stage could not be assessed.

Table III.1. Analytical and Spectral Data of the Complexes

Sl. No.	Complex	Anion	Colour (M.P/°C)	(calcd) found (%)		I. R. bands (C=C) cm ⁻¹		¹ H NMR	
				C	H	7	8	δ C ₅ H ₅	δ (-CH=C) ppm
1.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(PPh ₃) ₂]	PF ₆	T (160-165)	(66.7) 67.3	(4.24) 5.05	1640, 1622		4.5(s); 5.4(t)	
2.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(PPh ₃) ₂]	BF ₄	T (145)	(70.5) 69.9	(4.48) 4.2	1638, 1620		4.4(s); 5.3(t)	
3.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(PPh ₃) ₂]	BPh ₄	T (152)	(80.6) 80.1	(5.26) 5.41	1640, 1622		4.42(s); 5.34(t)	
4.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(AsPh ₃) ₂]	PF ₆	T (155-158)	(61.6) 62.09	(4.0) 4.7	1640, 1620		4.32(s); 5.3(s)	
5.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(AsPh ₃) ₂]	BF ₄	T (148-150)	(64.8) 65.1	(4.12) 4.6	1643, 1625		4.5(s); 5.4(s)	
6.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(AsPh ₃) ₂]	BPh ₄	T (150)	(75.28) 74.9	(4.9) 5.3	1638, 1622		4.6(s); 5.42(s)	
7.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(SbPh ₃) ₂]	PF ₆	B (155)	(56.9) 55.9	(3.7) 4.1	1640, 1620		5.17, 4.98(d); 5.45(s)	
8.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(SbPh ₃) ₂]	BF ₄	B (143)	(59.7) 60.2	(3.79) 3.9	1640, 1622		4.8, 4.89(d); 5.38(s)	
9.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)(SbPh ₃) ₂]	BPh ₄	T (143-145)	(70.3) 70.8	(4.58) 4.8	1642, 1625		4.9, 4.94(d); 5.4(s)	
10.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)dppe]	PF ₆	T (160-162)	(62.8) 63.1	(4.17) 4.62	1638, 1622		4.6(s); 5.3(t)	
11.	[Ru(η ⁵ -C ₅ H ₅)(C=CHR)dppe]	BF ₄	B (157-159)	(67.0) 67.5	(4.4) 4.76	1640, 1620		4.68(s); 5.26(t)	

...contd.

1	2	3	4	5	6	7	8
12.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{CHR})\text{dppm}]$	PF_6	T (158-160)	(62.5) 62.9	(4.0) 4.8	1642, 1620	4.7(s); 5.3(t)
13.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{CHR})\text{dppm}]$	BF_4	T (150-152)	(66.7) 67.0	(4.28) 4.5	1640, 1618	4.75(s); 5.2(t)
14.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{CHR})\text{dppe}]$	BPh_4	T (148)	(78.9) 78.1	(5.3) 5.5	1638, 1622	4.8(s); 5.38(t)
15.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{CHR})\text{dppm}]$	BPh_4	B (145)	(78.9) 78.3	(5.2) 5.71	1640, 1620	4.82(s); 5.4(t)
16.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{PPh}_3)_2]$		Y (130-135)	(77.3) 77.6	(4.9) 5.7	2000	4.5(s)
17.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{AsPh}_3)_2]$		Y (132)	(70.58) 71.1	(4.48) 4.9	2000	4.52(s)
18.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{SbPh}_3)_2]$		Y (135-138)	(64.5) 64.9	(4.1) 4.5	2020	4.3, 4.42(d)
19.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{dppe})]$		Y (152-155)	(74.5) 74.8	(4.9) 5.3	2010	4.5(s)
20.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{dppm})]$		Y (158-160)	(74.3) 74.9	(4.7) 4.32	2010	4.46(s)

R=pyrene group, dppe=1,2-bis(diphenylphosphino)ethane, dppm=1,2-bis(diphenylphosphino)methane,

T=tan, B=buff and Y=yellow.

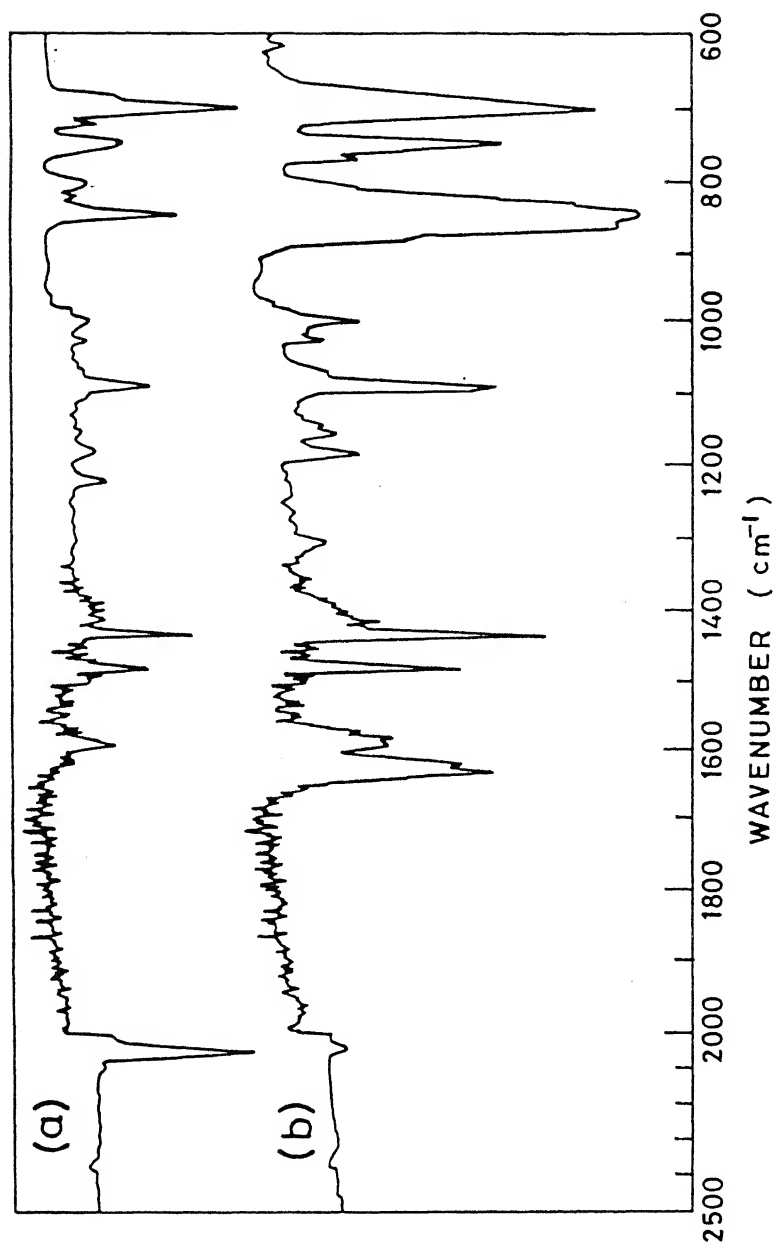


Fig.III.1. Infrared Spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{R})(\text{PPh}_3)_2]^+$,
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHR})(\text{PPh}_3)_2]^+\text{PF}_6^-$

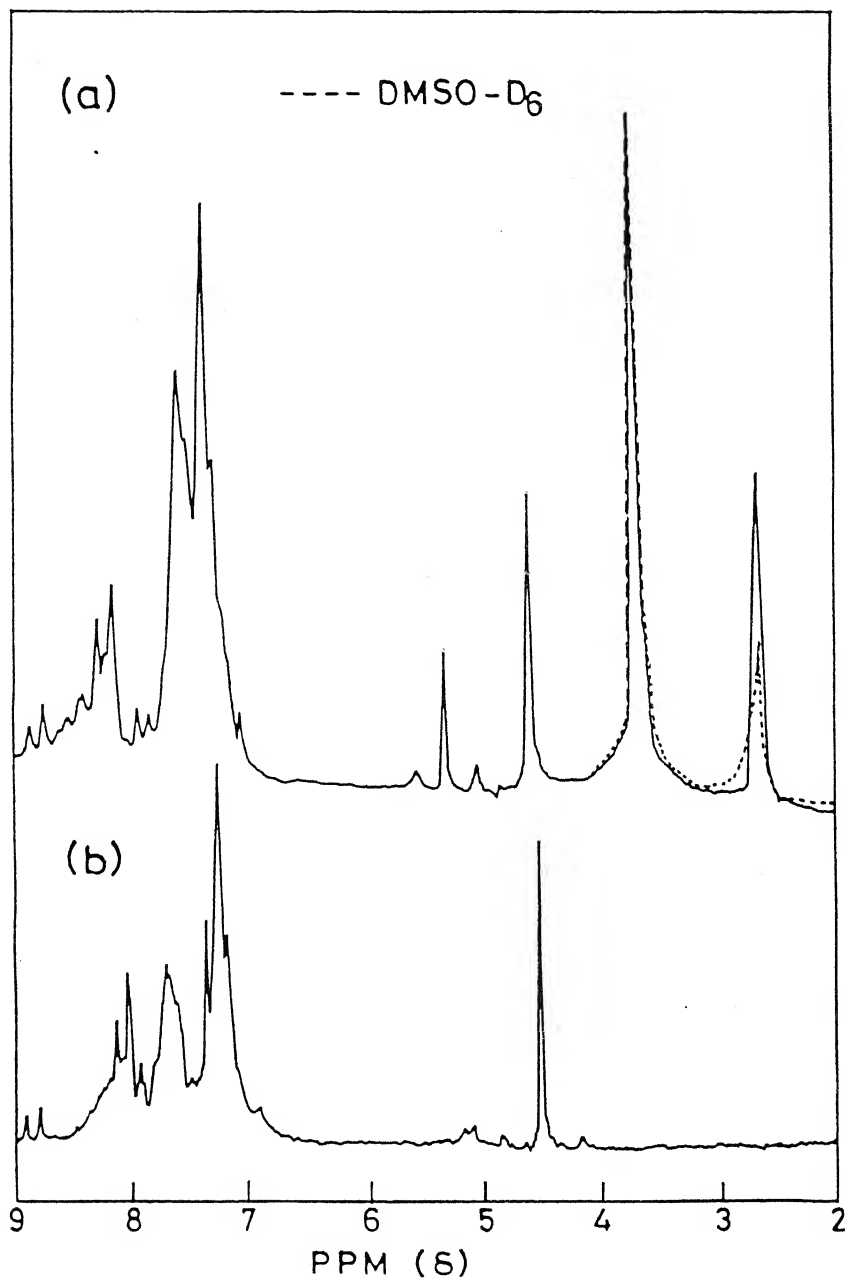


Fig.III.2. ^1H NMR Spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHR})-(\text{PPh}_3)_2]\text{PF}_6$, (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{R})(\text{PPh}_3)_2]$

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Chapter III

Part II: REACTIONS OF 1,7-OCTADIYNE AND 1,4-DICYANO- 2-BUTENE WITH CYCLOPENTADIENYL RUTHENIUM COMPLEXES: AN EXAMPLE OF ACETYLENE-ALLENE REARRANGEMENT IN INORGANIC COMPLEXES

Introduction

The reactions of a large number of metal complexes with 1-alkynes in presence of a base to yield corresponding acetylides have been reported.¹⁻⁵ Although the field spanning the chemistry of the transition metal alkylidene complexes is now well explored,^{6,7} high yield synthetic routes to alkylidene (vinylidene) $M=C=CR_2$ and allenylidene ($M=C=C=CR_2$) complexes using hydroxy substituted acetylenes have only recently developed.⁸⁻¹⁵ Work in the field to develop inorganic complexes as suitable alkyne oligomerisation catalysts for polymerization of simple diynes via the intermediacy of inter and intra molecular metallocycles is still continuing.¹⁶ It will therefore be in order to study reactions of terminal diynes with $[Ru(\eta^5-C_5H_5)(EPh_3)_2X]$ and its other substituted derivatives. In the course of our studies we aimed at the search to develop efficient and reproducible synthesis of either (1) bridged acetylide complexes,

or (2) allenylidene complexes by acetylene-allene rearrangement or (3) polymerized acetylene derivatives with metallocycles as intermediates. The second part of this chapter reports the synthesis of allenylidene complexes by interacting $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-ClL}_2]$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 1,7-octadiyne.

As a comparative study we have also carried out reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ with 1,4-dicyanobutene having terminal cyano groups, iso-electronic with $\text{-C}\equiv\text{CH}$ moiety. In 1,4-dicyano-2-butene the nucleophilic character of the nitrogen atom of cyano groups could be exploited to synthesize bridged metal complexes. We also report herein the results of these reactions. All the complexes have been characterized by elemental analyses and spectral (i.e., n.m.r) studies.

Experimental

All chemicals of chemically pure grade were used without further purification. Solvents were dried before use.¹⁷ The complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) were prepared by the literature methods¹⁸⁻²¹ 1,7-octadiyne and 1,4-dicyano-2-butene were obtained from the Aldrich. Analytical and spectral data of the products were obtained as described elsewhere.¹⁹

Preparation of Complexes

(a) Preparation of vinylidene complexes from 1,7-octadiyne

preparation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{L}_2)_2](\text{PF}_6)_2$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm (complex A))

A mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_1\text{L}_2\text{Cl}]$ (0.13 mmol), NH_4PF_6 (0.12 mmol) and a few drops of $\text{H-C}\equiv\text{C}-(\text{CH}_2)_4\text{-C}\equiv\text{C-H}$ (ca. 0.5 ml) in dry methanol (25 ml) was heated to reflux for about 3-4 h. The resulting deep red coloured solution was filtered and evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 (5 ml) and to the extract about 50 ml of petroleum ether was added, whereby a cream coloured precipitate was formed which was separated by centrifugation, washed several times with pet ether and dried under vacuum. It was analyzed for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})\text{L}_1\text{L}_2](\text{PF}_6)_2$ (yield, ca. 35 %).

The tetrafluoroborate salts of the complexes were obtained by a procedure similar to (a) except that about 0.18 mmol of NaBF_4 was added in place of NH_4PF_6 (yield, ca. 35 %).

(b) Preparation of alkynyl and allenylidene complexes from 1,7-octadiyne

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{L}_2)_2]$ (complex B) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{L}_2)_2]$ (complex C) ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm)

A mixture of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_1\text{L}_2]$ (100 mg, 0.13 mmol) and

$\text{H}-\text{C}\equiv\text{C}-(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{H}$ (0.5 ml) was heated in refluxing methanol (25 ml) for about an hour until the starting complex dissolved completely. To the deep red coloured solution, thus obtained, sodium methoxide (1 ml of a 1M solution in methanol) was added, whereupon a yellow coloured compound separated out. It was centrifuged out, washed with methanol and ether several times before drying in vacuum. This compound was obtained in very poor yields. It was analysed for $[(\eta^5-\text{C}_5\text{H}_5)_2\text{Ru}_2(\mu-\text{C}_8\text{H}_8)(\text{L}_2)_2]$ (complex B) (yield, ca. 10%).

The deep red filtrate was then evaporated to dryness under reduced pressure and the residue was extracted with 5 ml of CH_2Cl_2 . 40 ml of pet ether was added to the extract yielding a light pink precipitate of $[(\eta^5-\text{C}_5\text{H}_5)_2\text{Ru}_2(\mu-\text{C}_8\text{H}_6)(\text{L}_2)_2]$ (complex C) (yield, ca. 80%).

Complex (B) on dissolution in CH_2Cl_2 and passing through a short column of basic alumina using CH_2Cl_2 as eluent got converted to complex (C). The conversion was found to be 100 %.

(c) Reaction of trans 1,4-dicyano-2-butene with $[\text{Ru}(\eta^5-\text{C}_5\text{H}_5)\text{ClL}_2]$
(L = PPh_3 , AsPh_3 or SbPh_3 ; L_2 = dppe or dppm) in presence of
a suitable anion

A suspension of $[\text{Ru}(\eta^5-\text{C}_5\text{H}_5)\text{ClL}_2]$ (0.13 mmol), a salt of a suitable anion, (NH_4PF_6 or NaBF_4) (0.25 mmol) and $\text{NC}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{CN}$ (0.37 mmol) was taken in dry methanol (25 ml) and heated

to reflux for about 2 h, whereupon the suspension dissolved to give a bright yellow solution. The solution was concentrated slowly on a water bath. Yellow crystals separated out. These crystals were centrifuged, washed with methanol, diethyl ether and dried under vacuum. The complex was analysed for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ru}_2(\text{N-C}_6\text{H}_6\text{N}_2)(\text{L}_2)_2]\text{X}_2$ (complex D) (yield, ca. 38%).

Purification of products

All the products were purified by passing through a neutral alumina column. The compounds were dissolved in 5-10 ml of CH_2Cl_2 and passed through the column. The major band obtained was eluted with a 1:1 mixture of CH_2Cl_2 and CHCl_3 . The resulting solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 , and from the extract the complex was precipitated with petroleum ether, subsequently it was centrifuged, washed and dried.

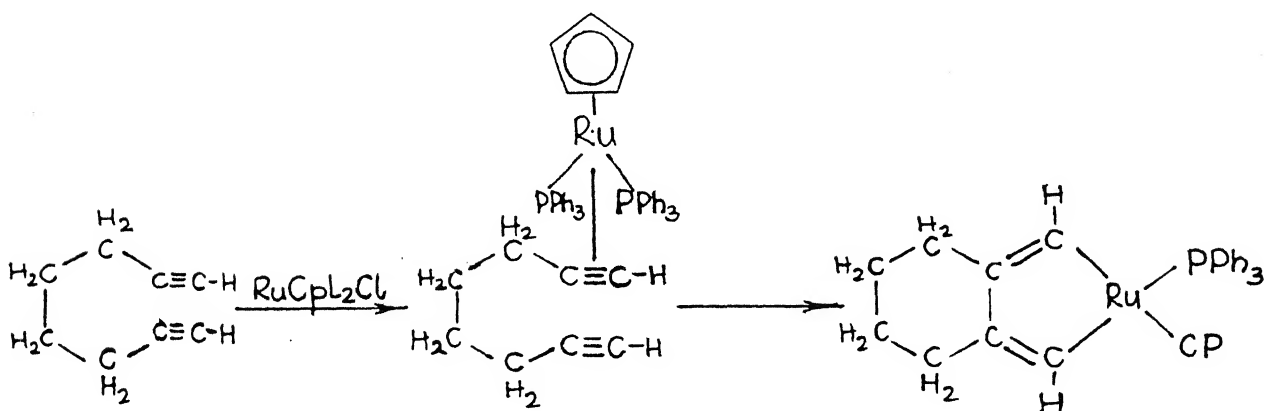
Results and Discussion

The analytical data of the complexes suggested that the binuclear cationic vinylidene complexes of ruthenium could be prepared in good yields by the reactions of 1,7-octadiyne in presence of large anion like PF_6^- . These complexes were found to be soluble in dichloromethane, acetone, THF, moderately soluble in benzene, methanol but insoluble in light petroleum and diethyl ether. The solubility of allenylidene complexes was found to be the same as that of vinylidene complexes. The alkynyl binuclear

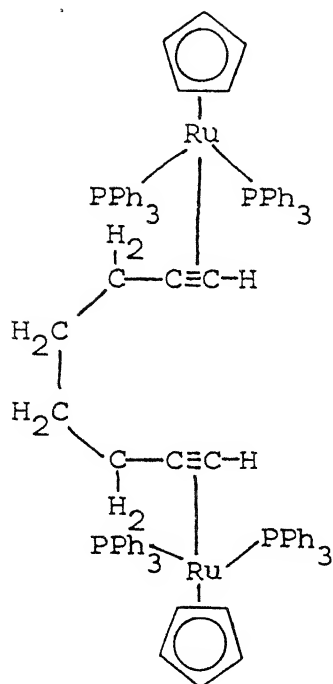
complexes however were found to be soluble in ether, moderately soluble in methanol. Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ with 1,4-dicyano-2-butene in the presence of a suitable anion BF_4^- or PF_6^- yielded bright yellow cationic binuclear complexes. Microanalytical data suggested the formula given in Table III.2. They are non hygroscopic, soluble in chloroform, dichloromethane, acetone, DMF, DMSO, insoluble in methanol light petroleum or diethyl ether. Their cationic behaviour was confirmed by cation exchange, in which they get absorbed. All attempts to prepare mononuclear complexes failed.

The reactions of 1,7-octadiyne with $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{X}]$ can take the following three of the many possible routes.

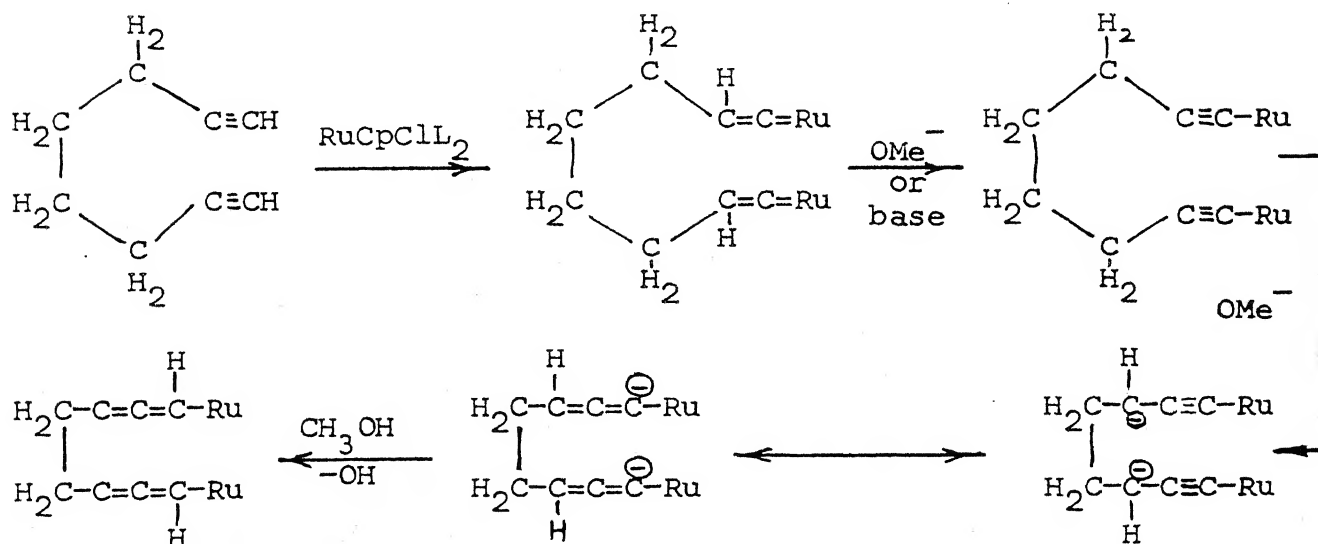
- (a) Formation of a bicyclic metallocycle containing a six membered ring with a possible intermediate of monoacetylene complex, leading to other organic products.



(b) Formation of π -bonded complex



(c) Formation of the vinylidene complex by proton 1,2-shift which is converted to acetylenic complex in presence of base, subsequently the latter undergoes acetylene-allene type of rearrangement forming an allene type of complex.



Scheme III.2

The first possible route could be tentatively ruled out on the following grounds (1) the analytical data will not match with the calculated one. (2) the metallocycle compounds are generally unstable and lead to the formation of organocyclic compounds. (3) the reactions with bases will yield different products compared to ones we have obtained.

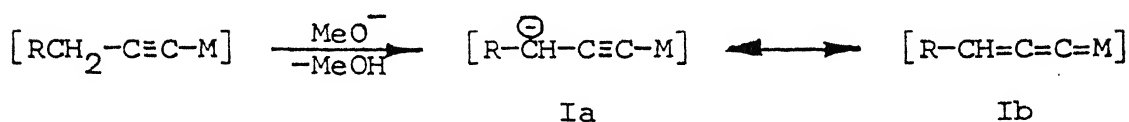
The second possibility could also be ruled out on the basis of the spectral data discussed in the later sections. Although we can not definitely decide the products resulting from its reaction with base, but the possibility of the ones that we have obtained is quite remote.

The third scheme which the reactions follow appears to be more likely since the observed analytical and spectral data of the reaction products match very well with those expected of the third route. Thus it appears certain that the reaction proceed via third route and later discussion will be based on similar grounds.

I.R. Spectra

The infra red spectra of the vinylidene binuclear complexes of 1,7-octadiyne (A) did not exhibit any band in the region 2100-1700 cm^{-1} indicating the absence of any triple bond $\text{-C}\equiv\text{C}$ present in the complexes. One extra band of medium intensity was however found at around 1640 cm^{-1} which has been assigned to the characteristic vibration of vinylidene moiety $\nu(\text{C}=\text{C})$. Strong absorptions

at 840 cm^{-1} or 1050 cm^{-1} are characteristic of PF_6^- or BF_4^- anions. The reactions of 1,7-octadiyne complexes in presence of a base, sodium methoxide gave allenylidene complexes (C) which exhibited a band at around 1970 cm^{-1} characteristic of allene group. The behaviour of the complexes of 1,7-octadiyne in presence of a base was found to be interestingly different from that of the mono-acetylenic complexes. Being an aliphatic dialkyne the two CH_2 groups directly attached to the triply bonded terminal acetylenic carbon atoms are quite prone to proton abstraction in the presence of bases like NaOMe generating a carbanion type of intermediate Ia in resonance with an allenic structure Ib.



The mechanism for the formation of an allenylidene complex as suggested above seemed quite logical as it was based on the principal of a stepwise acetylene-allene rearrangement involving carbanionic intermediates first proposed by Jacobs and coworkers.^{22,23} The process, also described as a base catalysed prototropic rearrangement, is basically an isomerisation reaction where triple bond migrates in presence of a base through an allene intermediate. In some cases the reaction is stopped at the allene stage. Thus the trapping of an allenylidene moiety in the 1,7-octadiyne complexes as shown by our experimental observations correlated very well with the established mechanism.

The alkynyl complexes (B) of 1,7-octadiyne isolated in very poor yields exhibited a band at around 2100 cm^{-1} characteristic of $\nu\text{C}\equiv\text{C}$ present in neutral complexes. Based on i.r. spectral studies (Table III.2) it is fairly certain that the reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{X}]$ proceeds according to the Scheme III.2 discussed above.

A prominent feature of the i.r. spectrum of 1,4-dicyano-2-butene ligand is presence of an intense and sharp band at 2280 cm^{-1} which has been assigned to $\nu(\text{CN})$. The binuclear cationic ruthenium complexes of 1,4-dicyanobutene displayed a single sharp band in the nitrile region at around 2260 cm^{-1} for νCN (Table III.2) which occurred at a lower frequency with respect to that in the free ligand. The presence of a single band in the i.r. suggested coordination of both the triply bonded $\text{C}\equiv\text{N}$ groups to two separate Ru(II) centres thus forming a symmetrical bridge between them. It also implies that the two $\text{C}\equiv\text{N}$ groups, being too far separated, do not interact to cause either broadening or splitting of the $\nu(\text{CN})$ bands. The decrease in the $\nu(\text{CN})$ stretching frequency observed in all these complexes could be attributed to donation of negative charge by Ru(II) to antibonding π^* orbitals of nitrile group in a linear metal nitrogen-carbon configuration. It is noteworthy that though $-\text{C}\equiv\text{N}$ is isoelectronic to $-\text{C}\equiv\text{CH}$, the allenylidene-allene type of arrangement $[-\overset{\text{H}}{\text{C}}=\text{C}=\text{NH}(\text{Ru})]$ \rightleftharpoons $[-\text{CH}_2-\text{C}\equiv\text{N}-\text{Ru}]$ has not been observed in nitrile complexes.

^1H N.M.R. Spectra

The conclusions deduced from the i.r. spectral data concerning the bonding modes in the complexes and their tentative structures have been further corroborated by the n.m.r. studies.

^1H n.m.r. spectra of the vinylidene complexes (A) of 1,7-octadiyne exhibited a signal around δ 5.2 ppm assigned to the single proton of the vinylidene group ($-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{CH}-\text{Ru}$), δ 1.0–2.5(m) CH_2 protons of the bridging octadiyne, δ 7.1–7.8 (EPh_3) and δ 4.8(s) ($\eta^5\text{-C}_5\text{H}_5$) protons. In the spectra of the allenylidene complexes (C), signals appeared at δ 5.1 ($\eta^5\text{-C}_5\text{H}_5$), around δ 5.6(s) (proton of the allene group ($-\overset{\text{H}}{\text{C}}=\text{C}=\text{C}=\text{Ru}$) (Fig. III.5b), besides the characteristic bands of CH_2 and phenyl protons in the expected region. In the spectra of neutral alkynyl complex (B), $\eta^5\text{-C}_5\text{H}_5$ protons exhibit a band at δ 4.4(s) but in a number of cases a solution of these complexes contained a mixture of alkynyl and allenylidene complexes in equilibrium exhibiting two types of $\eta^5\text{-C}_5\text{H}_5$ protons at δ 4.4 and δ 5.1. In the complexes of dppe or dppm we could however separate the alkynyl complexes from the allenylidene ones in which the $\eta^5\text{-C}_5\text{H}_5$ protons occurred at δ 5.0 (Fig. III.5), CH_2 protons of dppe or dppm around δ 2.0–2.5 as a doublet and CH_2 protons of octadiyne around δ 1.0–2.0. It appears that the changes in the position of the proton signals of $\eta^5\text{-C}_5\text{H}_5$ is very sensitive to the values of electron density at the metal centre. In cationic complexes protons are more

deshielded compared to neutral complexes and high electron density at metal centre shifts the proton signal towards high field side.

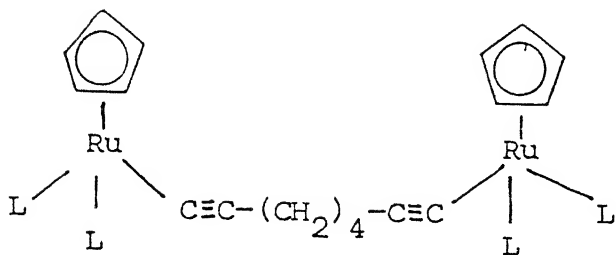
^1H n.m.r. spectra of 1,4-dicyanobutene complexes exhibited a single sharp band at δ 4.5, ($\eta^5\text{-C}_5\text{H}_5$ protons in case of PPh_3 or AsPh_3 complexes). In SbPh_3 complexes this band occurred around δ 4.65-4.9 (Fig. III.6). It showed a down field shift and was found to be splitted. The latter observation could be because of the interaction of the $\eta^5\text{-C}_5\text{H}_5$ protons with the bulky SbPh_3 groups slightly tilted in configuration. It is in accordance with our earlier observations.²⁰ The phenyl ring protons exhibited broad multiplets in the δ 7.1-7.7 ppm. In the absence of any π -back bonding from Ru(II) to 1,4-dicyanobutene ligand in the complexes, inductive effects due to -CN group exhibited a multiplet at δ 3.19 as compared to δ 3.18 in the free ligand. The olefinic (-CH=) protons were found to be more shielded in the complexes (ca. δ 5.14 m as compared to those in the free ligand (ca. δ 5.83)).

Although it is rather difficult to make a definite assignment of ^{13}C signals in the ^{13}C n.m.r. spectra of the complexes because of the presence of a number of signals. However one may expect the acetylide signals of medium intensity since quaternary carbon atoms generally exhibit longer relaxation time than protonated carbons and shows little Nuclear Overhauser Enhancement. This point has proved to be advantageous for the peak

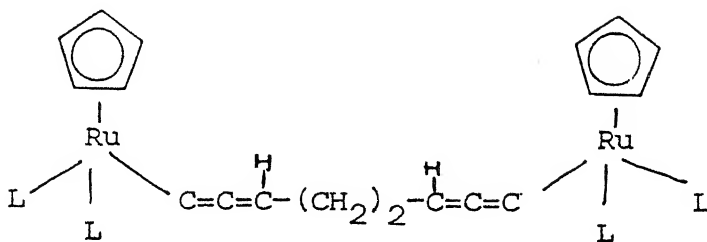
assignments of 1,7-octadiyne complexes. The most intense peak in the δ 80-90 ppm region has been found to be present at δ 88.9 ppm which has been assigned to CP carbon atoms (Table III.2). The signals for 1,7-octadiyne have occurred at the usual places (protonated carbons in the range δ 20-75 ppm), δ 91.5 ppm (Ru-C) and double and triple bonded carbon, in the range δ 90 and above). In the complexes (C) number of signals was a little more than the number of carbon atoms in octadiyne again indicating the allene-allenylidene equilibrium in solution, which is suggested by the ^1H n.m.r. and i.r. spectral data also. Furthermore deshielding of CP carbon atoms in the octadiyne complexes with respect to that in the parent complexes again suggest the sensitivity of the positions of ^{13}C signals on the electron density upon the Ru^{II} center. Since allene and allenylidene ligands are excellent π -acceptors,⁸ the electron density of Ru(II) will be reduced compared to that on the metal in the parent complexes,^{24,25} resulting in deshielding of cyclopentadienyl carbon. This further supports the sensitivity of the positions of signal of ^1H and ^{13}C in the n.m.r. spectra.

The ^{13}C n.m.r. spectra of 1,4-dicyanobutene exhibit signals around δ 19.4 ppm (CH_2), δ 86.2 ($\eta^5\text{-C}_5\text{H}_5$), a weak band at δ 83.4 ($\text{C}^{\text{H}}=\text{carbon}$) and δ 128.3-140.0 (EPh_3). The positions of these bands are expected ones for the CN bonded ruthenium complexes.

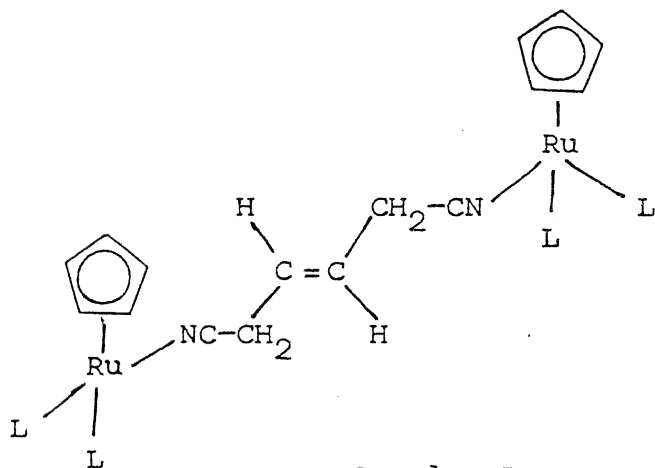
Based on the above analytical and spectral measurements, the following structures of the complexes are suggested.



Complex B



Complex C



Complex D

Table III.2. Analytical and Spectral Data of the Complexes.

Sl. No.	Complexes	Colour melting point/%	Analyses, found (calcd) %				Major i.r. bands				¹ H NMR (δ ppm)				¹³ C NMR (δ ppm) (C ₅ H ₅)
			C	H	N						-C≡C-H	H-C≡C-H	-C≡C- ⁵ IL-C ₅ H ₅		
1	2	3	4	5	6	7	8	9	10	11					
1	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{P})_4](\text{PF}_6)_2$	P (116-120°C)	60.5 (60.8)	5.5 (4.5)	-	1640	5.4	-	4.8	88.9					
2	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{P})_4](\text{BF}_4)_2$	YG (125)	63.9 (65.0)	5.7 (4.8)	-	1638	5.3	-	4.7	89.0					
3	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})\{\text{A}(\text{P})\}_2](\text{PF}_6)_2$	P (120)	58.4 (57.9)	4.9 (4.3)	-	1640	5.42	-	4.7	88.4					
4	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})\{\text{A}(\text{P})\}_2](\text{BF}_4)_2$	YG (125-130)	62.3 (61.8)	5.1 (4.6)	-	1642	5.3	-	4.8	88.5					
5	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{A})_4](\text{PF}_6)_2$	P (125)	56.0 (55.3)	5.0 (4.1)	-	1642	5.4	-	4.75	88.9					
6	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{A})_4](\text{BF}_4)_2$	YG (130)	58.7 (58.8)	5.2 (4.4)	-	1638	5.42	-	4.78	88.4					
7	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{dppe})_2](\text{PF}_6)_2$	P (150-152)	55.9 (55.1)	5.2 (4.5)	-	1640	5.5	-	4.9	89.0					
8	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{dppe})_2](\text{BF}_4)_2$	P (150)	60.3 (59.6)	5.3 (4.8)	-	1642	5.5	-	4.86	89.2					
9	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{dppm})_2](\text{PF}_6)_2$	YG (158)	54.9 (54.5)	4.9 (4.3)	-	1640	5.45	-	4.9	88.4					
10	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{dppm})_2](\text{BF}_4)_2$	YG (152)	60.0 (59.1)	5.2 (4.6)	-	1638	5.48	-	4.92	88.5					
11	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{P})_4]$	B (130)	70.9 (72.7)	5.7 (5.2)	-	2100	-	-	4.4	87.8					
12	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)\{\text{A}(\text{P})\}_2]$	B (128-130)	69.3 (68.7)	5.4 (4.9)	-	2095	-	-	4.42	87.4					
13	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{A})_4]$	B (125)	64.3 (65.0)	5.3 (4.7)	-	2100	-	-	4.4	87.9					
14	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{dppe})_2]$	B (140)	69.4 (68.2)	6.0 (5.4)	-	-	-	-	4.95	87.8					

...contd.

Table III.2 (contd.)

1	2	3	4	5	6	7	8	9	10	11
15	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{P})_4]$	F (140)	71.7 (72.8)	4.8 (5.2)	-	1970	-	5.6	5.1	86.8
16	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)\{\text{I}(\text{A})(\text{P})\}_2]$	F (142)	69.2 (68.8)	5.0 (4.7)	-	1968	-	5.6	5.0(s)	87.2
17	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{A})_4]$	F (138-140)	66.1 (65.2)	5.1 (4.4)	-	1970	-	5.58	5.1(s)	87.6
18	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{dppe})_2]$	F (158)	68.4 (69.1)	5.0 (5.5)	-	1980	-	5.6	5.0(s)	87.0
19	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{dppm})_2]$	F (153)	68.8 (68.0)	5.5 (5.0)	-	1970	-	5.5	5.2(s)	87.6
20	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{P})_4](\text{PF}_6)_2$	Y (180)	58.9 (59.4)	4.1 (4.3)	1.9 (1.6)	2265	-	-	4.5(s)	86.2
21	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{P})_4](\text{BF}_4)_2$	Y (98)	64.2 (63.6)	4.9 (4.6)	1.5 (1.7)	2260	-	-	4.5(s)	86.0
22	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)\{\text{I}(\text{A})(\text{P})\}_2](\text{PF}_6)_2$	Y (176)	57.0 (56.6)	4.7 (4.1)	1.8 (1.5)	2260	-	-	4.54	86.4
23	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)\{\text{I}(\text{A})(\text{P})\}_2](\text{BF}_4)_2$	Y (110)	61.3 (60.4)	4.7 (4.3)	1.9 (1.6)	2265	-	-	4.54(s)	86.2
24	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{A})_4](\text{PF}_6)_2$	Y (175-178)	54.6 (54.1)	4.3 (3.9)	1.2 (1.4)	2260	-	-	4.6(s)	86.2
25	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{A})_4](\text{BF}_4)_2$	Y (110-112)	56.2 (57.5)	4.6 (4.1)	1.9 (1.5)	2255	-	-	4.6(s)	85.8
26	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{sb})_4](\text{PF}_6)_2$	Y (168)	48.9 (49.3)	3.8 (3.5)	1.6 (1.3)	2260	-	-	4.7-4.9(m)	86.0
27	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{sb})_4](\text{BF}_4)_2$	Y (165)	53.4 (52.2)	4.6 (3.8)	1.7 (1.4)	2255	-	-	4.6-4.7(m)	86.4
28	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{dppe})_2](\text{PF}_6)_2$	Y (160-163)	53.9	4.8	2.2	2260	-	-	4.9(s)	86.2
29	$[(\eta^5\text{-C}_5\text{H}_5)_2(\text{Ru})_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{dppe})_2](\text{BF}_4)_2$	Y (138-140)	58.2 (57.9)	4.9 (4.5)	1.6 (1.9)	2255	-	-	4.8(s)	86.2

...contd.

Table III.2(contd.)

1	2	3	4	5	6	7	8	9	10	11
30	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{dppm})_2](\text{PF}_6)_2$	Y (170-172)	53.3 (52.9)	4.7 (4.0)	1.4 (1.9)	2260	-	-	4.84(s)	86.0

P = PPh_3 ; A = AsPh_3 ; Sb = SbPh_3 ; dppe = 1,2-bis(diphenylphosphinoethane); dppm = 1,2-bis(diphenylphosphinoethane);
 C_8H_{10} = 1,7-octadiyne; $\text{C}_6\text{H}_6\text{N}_2$ = 1,4-dicyano-2-butene; P = Pink; YG = Yellowish green; B = Brownish yellow; F = Fawn;
 Y = Yellow

Characteristic i.r. bands due to $(\text{EPh}_3, \text{dppe or dppm}) = 1485, 1440, 1088, 840, 747, 698$.

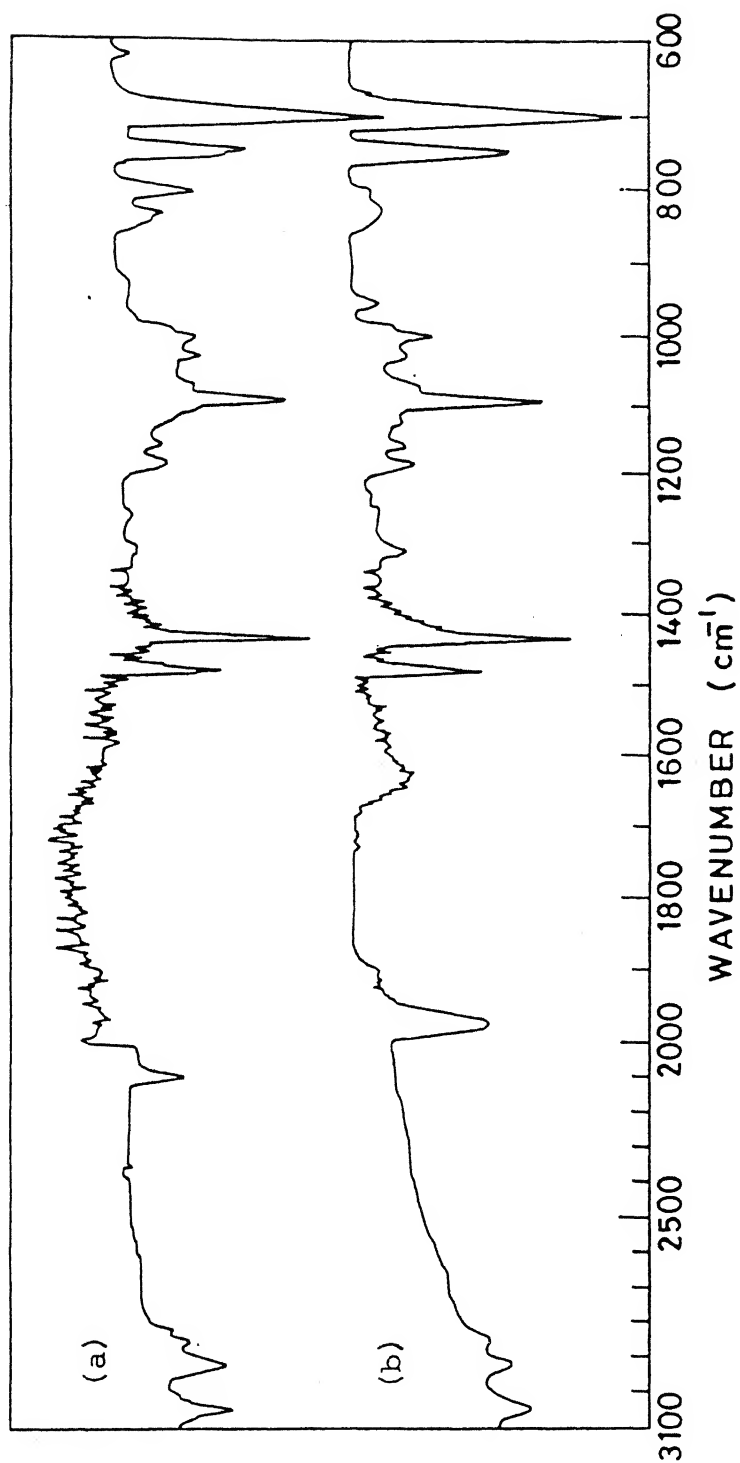


Fig. III.3. I.R. Spectra of (a) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{PPh}_3)_4]$,
 (b) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{PPh}_3)_4]$



Fig.III.5. ^1H NMR Spectra of
 (a) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{PPh}_3)_4](\text{PF}_6)_2$
 (b) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{PPh}_3)_4]$
 (c) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{dppe})_2]$

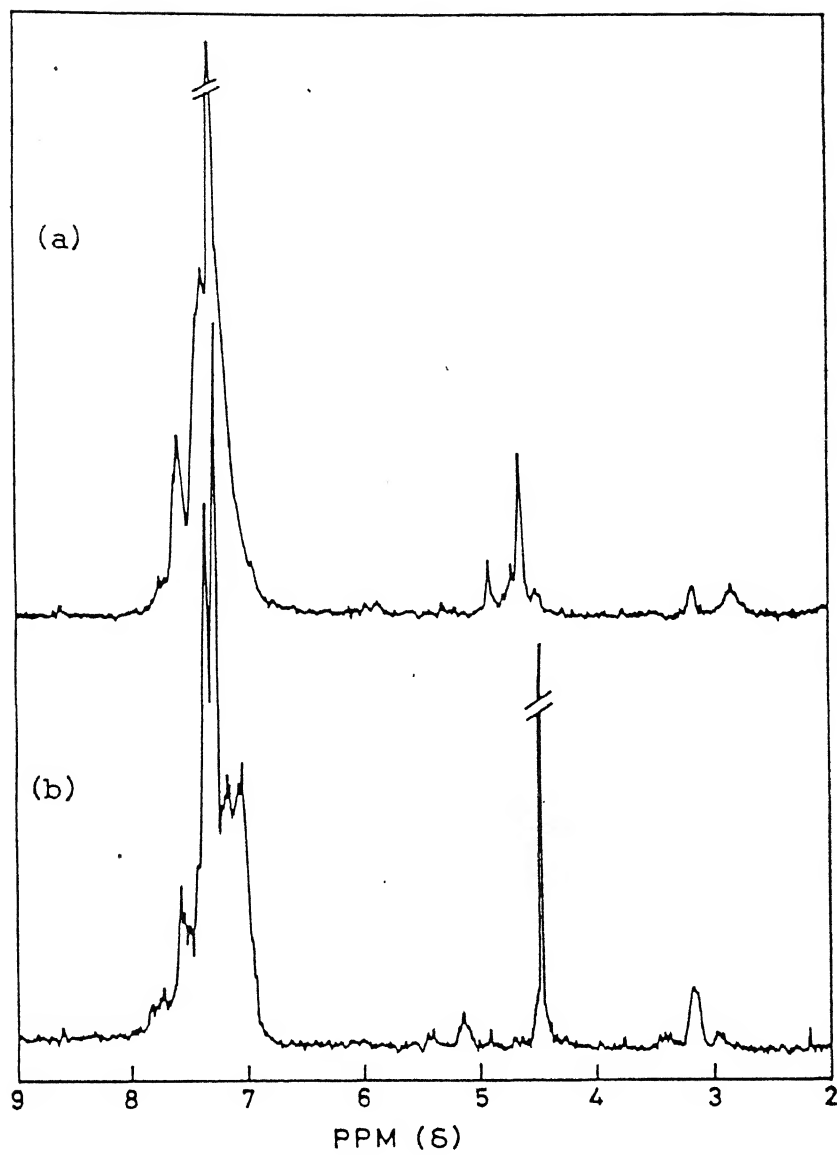


Fig.III.6. ^1H NMR Spectra of
 (a) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{SbPh}_3)_4]$,
 (b) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{PPh}_3)_4]$

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CHAPTER IV

PREPARATION AND STRUCTURAL PROPERTIES OF MONONUCLEAR AND BINUCLEAR Ru(II) CYCLOPENTADIENYL COMPLEXES WITH 4-CYANOPYRIDINE AND 4-CYANOPYRIDINE 1-OXIDE

Introduction

In extending our studies related to the properties of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Cl}]$ ($\text{E} = \text{P, As or Sb}$) we became interested in the interaction of these molecules with 4-cyanopyridine and its corresponding oxide. Though there have appeared several detailed reports concerning the complexes of these ligands with metal ions,¹⁻¹³ our primary interest in undertaking such a study was (a) to ascertain the relative donor capabilities of these ligands, (b) to examine the nature of ruthenium(II) orbitals (d^6) interaction with the low lying vacant ligand orbitals while the set of "spectator" ligands are also donor, and (c) to investigate the possibility of formation of cyclopentadienyl containing Ru(II) bi and/or polynuclear bridged complexes. We anticipate some futuristic value of these results while investigating the extent of metal orbital participation in the back bonding to

a particular ligand when a set of ''spectator'' ligands are being slowly changed from acceptor to donors.

This chapter describes the characterized products of the reactions of 4-cyanopyridine and 4-cyanopyridine 1-oxide with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Cl}]$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})\text{Cl}]$ ($\text{E} = \text{P}$ or As ; $\text{L-L} = \text{dppe}$ or dppm). Their structural properties have been discussed and the influence of the asymmetric nature of these ligands on the structure of the complexes has been assessed.

Experimental Section

(i) Materials

All chemically pure reagents and dry solvents¹⁴ were used in the reactions. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{EPh}_3)_2]$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})\text{Cl}]$ ($\text{E} = \text{P}$ or As ; $\text{L-L} = \text{dppe}$ or dppm) were prepared by the literature methods.¹⁵⁻¹⁸ 4-Cyanopyridine and 4-cyanopyridine 1-oxide (Aldrich) were purified prior to their use by recrystallisation from 95 % ethanol. HPLC grade deaerated acetonitrile (distilled over KMnO_4 and P_2O_5) for spectral, electrochemical measurements and spectroscopic grade solvents for the study of solvatochromism and conductivity measurements have been used.

(ii) Instrumentation

Elemental analyses were performed at the Microanalytical laboratory of I.I.T. Kanpur, India.

Infra red spectra of solid samples were taken as KBr pellets on Perkin Elmer I.R. Spectrophotometer model 580. ^1H n.m.r. spectra were recorded on a EM-390,90 MHz NMR or Bruker WP-80 spectrophotometer.

^{13}C n.m.r. spectra of the complexes were recorded on a JEOL FT-90 spectrophotometer.

Electronic absorption spectra were recorded on a Shimadzu model u.v. - 190 double beam spectrophotometer with matching quartz cells.

Conductivity measurements were carried out in dry nitromethane using an Elico conductivity bridge type CM82T.

Cyclic voltammograms of the samples were obtained in acetonitrile solution using TBAP as supporting electrolyte. The c.v. measurements were performed using a three electrode potentiostatic circuit and a MPI model MP-1042 voltammetry controller and platomic MF 715 X-Y recorder. A Beckman Pt Electrode, a Pt wire counter electrode and saturated electrode constitute the three electrode assembly. All the potentials are referred to SCE.

Preparation of Complexes

Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 4-cyanopyridine and 4-cyanopyridine 1-oxide.

- (A) Preparation of the Complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2(4\text{-CNpy})]\text{X}$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2(4\text{-CNpyo})]\text{X}$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X}^- = \text{Cl}^-$, PF_6^- or BPh_4^-)

In a typical reaction addition of 4-cyanopyridine (0.57 mmol) or 4-cyanopyridine 1-oxide (0.33 mmol) to a suspension of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Cl}]$ (0.13 mmol) in methanol (50 ml), followed by heating under reflux for sometime (Table IV.1a), yielded a yellow coloured solution. It was filtered, evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. Addition of about 50 ml of petroleum ether to the extract yielded a microcrystalline product. It was separated by centrifugation, washed several times with petroleum ether and dried under vacuum. The chloro complex thus obtained, was purified by neutral alumina column chromatography (25 cm). It was dissolved in methanol (10ml) and passed through column. The major band was eluted by a 1:1 mixture of methanol and acetone. The resulting solution was evaporated to dryness and the residue was extracted with dichloromethane. From the extract the complex was precipitated by petroleum ether. It was separated by centrifugation, washed several times with petroleum ether and dried in vacuum. It was analysed for $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2(4\text{-CNpy})]\text{Cl}$ (yield, ca. 40 %) or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2(4\text{-CNpyo})]\text{Cl}$ (yield, ca. 50 %).

The corresponding tetraphenylborate and hexafluorophosphate salts of the monomeric cyanopyridine and cyanopyridine 1-oxide complexes were obtained by precipitating the complexes by adding NaBPh_4 (0.06 mmol) and NH_4PF_6 (0.12 mmol) respectively to a solution of the chloro complexes in 20 ml methanol, followed by a brief stirring for about 20 minutes. These were filtered, washed several times with methanol, and ether. The compounds were purified by dissolving them in 5 ml of dichloromethane and eluting on a neutral alumina column (25 cm) by a 1:1 mixture of CH_2Cl_2 and acetone. The eluent was dried under vacuum, the residue was extracted with CH_2Cl_2 and from the extract the complex was precipitated by petroleum ether. The precipitates after washing and drying were analysed for $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2(4\text{-CNpy})]\text{X}$ (yield, ca. 40 %) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2(4\text{-CNpyo})]\text{X}$ (yield, ca. 45 %) ($\text{X} = \text{BPh}_4^-$ or PF_6^-).

(B) Preparation of the dimeric complexes $[(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2\text{-Ru-4-CNpy-RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2\text{Ru-4-CNpyo-RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ ($\text{L}, \text{L}' = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2, \text{L}_2' = \text{dppe}$ or dppm ; $\text{X} = \text{BPh}_4^-$ or PF_6^-)

A typical reaction procedure is as follows. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{ClL}_2]$ (0.13 mmol) was added to a (50 ml) methanolic solution of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2'(4\text{-CNpy})]\text{Cl}$ (0.13 mmol) or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2'(4\text{-CNpyo})]\text{Cl}$ (0.13 mmol). The resulting mixture was stirred overnight, whereupon the starting complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2\text{Cl}]$ gradually

dissolved. The resulting solution was filtered and NaBPh_4 (0.12 mmol) was added to the filtrate, followed by stirring for a brief period. The precipitated complex separated by centrifugation, washed with methanol and purified chromatographically on a neutral alumina column.

The corresponding hexafluorophosphate salt of the binuclear complex was obtained by adding NH_4PF_6 (0.12 mmol) in place of NaBPh_4 , followed by stirring the solution for half an hour. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 and PF_6^- complex was precipitated by adding petroleum ether to the extract. BPh_4 or PF_6 salts of binuclear cyanopyridine or cyanopyridine 1-oxide was dissolved in about 5-10 ml of CH_2Cl_2 and passed through a neutral alumina column for purification. The major band was eluted by 1:1 mixture of CH_2Cl_2 and acetone. The eluent was evaporated to dryness and the complex was obtained by extracting the residue with CH_2Cl_2 and precipitating it with petroleum ether. It was centrifuged, washed several times with petroleum ether and dried in vacuo. It was analysed for $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Ru-4CNpyRuL}_2'(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ (yield, ca. 35 %) or $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Ru4CNpyoRuL}_2'(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ (yield, ca. 30 %) ($\text{X} = \text{BPh}_4^-$ or PF_6^-).

Results and Discussion

Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 4-cyanopyridine in presence of suitable anions (PF_6^- or BPh_4^-) yielded reddish brown mononuclear, maroon coloured binuclear and with 4-cyanopyridine 1-oxide, bright yellow, mononuclear and yellowish brown, binuclear cationic complexes. Micro-analytical data suggest the formulae given in (Table IV.1a and IV.1b). They are non-hygroscopic, readily soluble in chloroform, dichloromethane, acetone, acetonitrile, benzene and other organic solvents, insoluble in light petroleum and diethyl ether. The chloride salts are readily soluble, while those of PF_6^- or BPh_4^- salts, only slightly soluble in methanol. All the complexes get adsorbed in the cationic ion-exchanger suggesting their cationic nature.

Conductivity measurements

The electrolyte behaviour of the complexes were determined by their conductivity measurements in nitromethane using Feltham and Hayter procedure.¹⁹ From the measured values of the equivalent conductance (λ_e) in a concentration range of $10^{-2} - 10^{-4}$ equiv l^{-1} , λ_o was determined by extrapolating the straight lines (Fig. IV.1b) and subsequently values of $(\lambda_o - \lambda_e)$ (Fig. IV.1a) were plotted as a function of \sqrt{c} .²⁰⁻²² The respective slopes of the mono (216) and binuclear (420) complexes of the straight

lines for the 4-cyanopyridine complexes compared very well with those of the Feltham's values for 1:1 and 1:2 species in nitromethane.^{23,24} The corresponding slopes (358 and 728) for 4-cyanopyridine 1-oxide complexes, though a little high, also fall well within the range reported by them for 1:1 and 1:2 electrolytes.

I.R. Spectra

The shifts in the position of $\nu(\text{CN})$ and pyridine ring vibrations have been used to elucidate the site of coordination of the cyanopyridines. Coordination through nitrogen of the nitrile group should result in an increase in $\nu(\text{CN})$, while that, through pyridine nitrogen should lead to characteristic shifts in positions of pyridine ring vibrations without much change in the position of $\nu(\text{CN})$.

The i.r. spectra of all mononuclear complexes of cyanopyridine and its oxide exhibited bands of $\nu(\text{C}\equiv\text{N})$ around 2240 cm^{-1} (Table IV.1) (CN for free ligand = 2243 cm^{-1}). It, thus suggested the linkage of ruthenium through the aromatic nitrogen of 4-cyanopyridine and through oxygen of NO group of 4-cyanopyridine 1-oxide, in keeping with the earlier observations.^{7,11-13,25-28} An insignificant shift ($\pm 3\text{ cm}^{-1}$) in the positions of $\nu(\text{CN})$ is not unexpected which could arise by both resonance and electronic effects (π back bonding) due to bonding with the metal ion center.

Further support of bonding of ruthenium to aromatic nitrogen of cyanopyridine complexes comes from the blue shifts in the positions of $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ of cyanopyridines in the region 1400 to 1600 cm^{-1} .^{5,7,28}

In monomeric 4-cyanopyridine 1-oxide complexes the oxygen atom of the N-oxide group having partial negative charge got coordinated to Ru(II) nucleus. The contributing resonance structure of 4-cyanopyridine 1-oxide may be shown by a dipolar representation indicating charge separation and the polar character of the N-O bond where the oxygen atom is regarded as an addition to the molecule of 4-cyanopyridine. The NO stretching vibration in the complexes appeared at higher frequency relative to that in the free 4-cyanopyridine 1-oxide (1280 cm^{-1}). Bands due to $\nu(\text{NO})$ in monomeric complexes appeared around 1305 cm^{-1} (Fig. IV.3). The blue shift indicated its coordination to the metal centre. In dimeric complexes in which the uncoordinated CN group of the monomeric complexes got coordinated to another ruthenium center, a decrease in the position of $\nu(\text{CN})$ (2232 cm^{-1}) relative to that in the free ligand was observed.²⁹ (Fig. IV.2c). The reason for this expected decrease could be attributed to the metal $(d\pi) \longrightarrow$ ligand π^* back bonding.

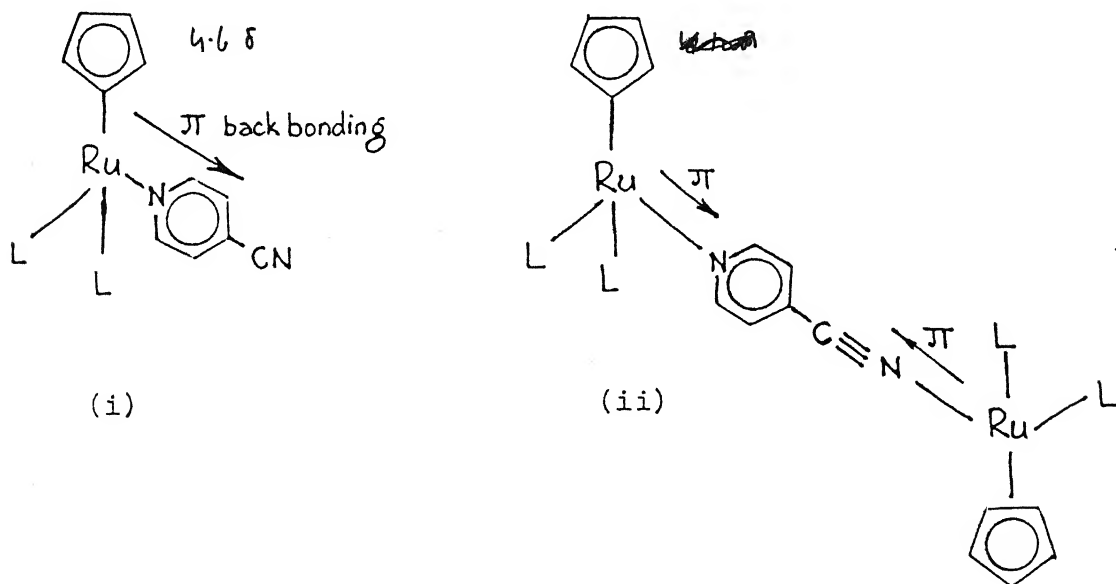
^1H N.M.R. Spectra

In the ^1H n.m.r. spectra of monomeric 4-CNpy and 4-CNpy

1-oxide complexes with $\text{PPh}_3/\text{AsPh}_3$ as coligands, $\eta^5\text{-C}_5\text{H}_5$ protons appeared as a singlet around δ 4.6, whereas in complexes containing dppe or dppm, around δ 4.9 (Table IV.1). The downfield shift of $\eta^5\text{-C}_5\text{H}_5$ protons relative to the starting complexes (δ 4.1 in $\text{PPh}_3/\text{AsPh}_3$; δ 4.5 in dppe/dppm) could result from the change of electron density on ruthenium because of backbonding from metal to 4-CNpy and more so because of the presence of a strong electron withdrawing -CN group substituted in the para position of the pyridine ring. The electron withdrawing as well as the conjugative ability of the -CN pulls the electron density from the pyridine nucleus towards itself, effecting the electron deficiency on the ruthenium metal. It may consequently lead to a pull of more electrons of C_5H_5 towards ruthenium centre resulting in deshielding of C_5H_5 protons.

In binuclear cyanopyridine cationic complexes, $\eta^5\text{-C}_5\text{H}_5$ protons resonate around δ 4.3 and δ 4.75 as two separate peaks suggesting a difference in the local electron density on the protons of the two $\eta^5\text{-C}_5\text{H}_5$ molecules present in the binuclear complexes (Fig. IV.4a). This could arise because of the difference in the nature of M-L bonding of two ruthenium centres. In complexes of 4-CNpy 1-oxide, the signal for C_5H_5 protons appeared as a broad singlet around δ 4.7 (Fig. IV.4b). Since the difference in the positions of two signals in binuclear complexes should be sensitive to the nature of L, it is therefore possible that the

two resonances in the 4-CNpy 1-oxide complexes appeared at nearly similar positions, resulting in the signal broadening. Furthermore the signals in binuclear complexes appeared at higher field with respect to those in mononuclear ones. One could anticipate this behaviour if one considers the fact that the two Ru(II) ions in a binuclear complex compete to donate the electron density to 4-CNpy (or 4-CNpy 1-oxide) through π -back bonding both from cyano nitrogen and aromatic nitrogen (or through oxygen of $N \rightarrow O$ moiety). This competition would result in the net reduction of the π -bonding effect on the C_5H_5 protons (Fig. A) in binuclear complexes compared to that in mononuclear ones (ii and i respectively).



(Fig A)

The signals for the α -protons of the pyridine were observed towards higher field (δ 8.3-8.5) in both mono nuclear and binuclear complexes of 4-CNpy and 4-CNpy 1-oxide relative to ones reported for the free 4-cyanopyridine ligand (δ 9.05).³⁰⁻³² This upfield shift is ascribed to the 'paramagnetic' anisotropy of Ru(II) arising because of temperature independent paramagnetism expected of the metal centre.³⁰ The difference in the signal positions of the cyanopyridine and cyanopyridine 1-oxide complexes may perhaps be caused by the variation in the 'paramagnetic' anisotropic effect. It also suggested that a degree of $d\pi$ - π backbonding also influences the chemical shifts of the hydrogens. The β -protons in most of these complexes exhibited shifts towards higher field side (δ 7.0-7.9). Since this region was found to be dominated by broad multiplets of aromatic phenyl protons of PPh_3 , $AsPh_3$, dppe or dppm coligands, the pyridine proton signals could not be distinguished from them. The experimental observations of the upfield shift in these protons, could again be explained due to the higher shielding effect caused by the enhanced and stronger π -backbonding from the Ru(II) to cyanopyridine group.

^{13}C N.M.R.

The ^{13}C n.m.r. spectra of these complexes also support the conclusions arrived at from those of proton n.m.r. The $\eta^5-C_5H_5$ carbons in the mononuclear 4-CNpy 1-oxide complexes appeared as

singlet (δ 84.0) (Fig. IV.5), towards the downfield side relative to C_5H_5 carbons (δ 81.5) in the starting complexes. In binuclear complexes with $PPh_3/AsPh_3$ as coligands the spectra exhibited two signals around δ 83.0 and δ 84.5 and in those with $dppe/dppm$ as coligands, around δ 81.0 and δ 82.5 (Fig. IV.6). The phenyl carbons in all these complexes showed sharp multiplets in the expected region for aromatic carbons, (ca. δ 128.0-137). The cyanide carbon ($-CN$) underwent a downfield shift both in mono and binuclear complexes (δ 119.6, sharp singlet in the mononuclear and δ 121.5 in the binuclear complexes) compared to the value in the free ligand (δ 117.6). This downfield shift indicated deshielding of the carbon atoms on coordination to the metal atom. Coordination of 4-CNpy or 4-CNpy 1-oxide resulted in an upfield shift of the pyridine ring carbons (δ 145 and δ 140) relative to the free ligand (δ 150.5). Though the signals arising from β and γ carbons could not be distinguished from the phenyl carbons in all the complexes, but in a few complexes signals due to γ -carbon appeared in the upfield region with respect to the ones found in 4-CNpy (β = 127; γ = 121.4) or 4-CNpy 1-oxide. The shielding of all the carbon atoms on coordination is not unexpected because the factors like polarization of the N-C bond due to σ bonding at pyridine nitrogen, metal centred anisotropic diamagnetic currents and increased electron density due to the π bonding will have a net shielding contribution to the carbon atoms of the pyridine ring.

^{31}P N.M.R.

^{31}P n.m.r. of the 4-cyanopyridine and 4-cyanopyridine 1-oxide complexes exhibited a single sharp signal around δ 41.5 and δ 41.9 respectively for the PPh_3 phosphorus (Fig. IV.7a). Similarly in dppe complexes a single sharp peak appeared at δ 80.4 for the diphos phosphorus (Fig. IV.7b). The deshielding of phosphorus might be caused by relatively less donation of electrons from metal to phosphorus through back bonding. It suggests that the degree of $d\pi$ - $p\pi$ backbonding influences the chemical shift of the phosphorus atoms and there exists a competition of π -electrons between 4-CNpy or 4-CNpy 1-oxide and other ligands supporting the ^1H and ^{13}C n.m.r. spectral conclusions.

Electronic Absorption Spectra

The low spin d^6 configuration of both the mononuclear and binuclear series of complexes provide filled orbitals of proper symmetry on Ru(II) to interact with the relatively low energy unoccupied π^* orbitals on the pyridine ring of 4-cyanopyridine or 4-cyanopyridine 1-oxide ligands. One should, therefore, expect a band attributable to MLCT transition ($t_{2g} \longrightarrow \pi^*$) in the complexes. Furthermore the energy of these transitions should vary with the nature of the ligand acting as a π -acceptor. The presence of an electron withdrawing substituent like $-\text{CN}$ group, in the 4-position of the pyridine and pyridine 1-oxide should

decrease the energy of the transition, causing a red shift in the MLCT maximum as well as greater ground state delocalisation of the $d\pi$ electron density into ligand (π -back bonding), while the electron donating group on pyridine ring should increase the transition energy.^{34,35} The electronic bands and their assignments for 4-CNpy complexes in various solvents are shown in Table IV.3. A band, around 450 nm has been assigned to MLCT transition ($t_{2g}Ru(II) \rightarrow \pi^*$) ligand of 4-CNpy (Fig. IV.8). The λ_{max} and the ϵ_{max} values correlated very well with those of the literature known pyridine bound 4-CNpy complexes of Ru(II) and Fe(II).⁵⁻⁷ The bonding of Ru(II) with aromatic nitrogen is supported by the fact that 485 nm band in our complexes appeared at lower energy compared to that in $[(\eta^5-C_5H_5)Ru(PPh_3)(Py)Cl]$ (465 nm) because of the electron withdrawing property of the CN group.³⁴⁻³⁶ Further support of the bonding comes from the fact that aromatic nitrogen bonded complexes always absorb at a longer wavelength compared to nitrile bound complexes.

In the spectra of the binuclear cationic complexes of the 4-CNpy there is a slight shift of λ_{max} towards higher frequencies in a few solvents (Table IV.3a). In some solvents λ_{max} remains unaltered. (A slight decrease was also observed in the position of λ_{max} in one or two solvents with respect to the mononuclear cationic 4-CNpy complexes. This 'anomalous' behaviour could be explained on the basis of asymmetrical nature of the bridging

ligand) π -back bonding from $\text{Ru}^{\text{a}}(\text{II})$ to the pyridine ring must raise the energy of the π^* orbitals of the nitrile end of the 4-CNpy, while the π -back bonding from $\text{Ru}^{\text{b}}(\text{II})$ to NC group should also raise the energy of the pyridine π^* orbitals. Because the energy of the MLCT transition is related to that of LUMO of the ligand, the increase in energy of the π^* orbital by both electron transfers from the metal centres should result in the shift of MLCT bands towards higher frequencies with respect to mononuclear complexes.

The MLCT absorptions exhibited solvatochromic effect. Various parameters like donor number (DN), Reichardt Dimroth parameter (ET), $1/\text{Dop} - 1/\text{Ds}$, E_{MLCT}^* , etc. have been defined³⁷⁻⁴⁰ and correlated with the absorption energies of MLCT transitions. Fig. IV.11 to IV.16 display these representative plots. They all show an excellent linear correlation between the variation of the MLCT band positions with the solvent polarity. The donor number plots show negative slope suggesting the decrease in the energy of the transition as the donor property of the solvent increases and the intercepts give the energy of the transition when the compound is dissolved in dichloroethane. Further a linear relationship is expected between the MLCT band positions and χ_{outer} assuming the applicability of Hush model⁴¹⁻⁴³ in these systems. Accordingly the energy of MLCT band which ought to be related to the Frank Condon term (χ_{inner}) and the solvent

reorientation properties (χ_{outer}) by the equation $E_{\text{op}} = \chi_{\text{inner}} + \chi_{\text{outer}} + E'_{\text{op}}$ should show linearity with the (χ_{outer}). The χ_{outer} can be calculated by using the relationship $\chi_{\text{outer}} = (\Delta e)^2 (1/2 a_1 + 1/2 a_2 - 1/r) (1/D_{\text{op}} - 1/D_{\text{s}})$. (Δe is charge transferred, D_{op} and D_{s} , the optic and the static dielectric constants of the medium, a_1 , a_2 and r , radii of the electron donor, acceptor and distance separating them). Fig. IV.16 shows the plot of E_{MLCT} vs $(1/D_{\text{op}} - 1/D_{\text{s}})$ for two representative compounds. This shows somewhat satisfactory relationship for both mononuclear and binuclear 4-CNpy 1-oxide complexes. The generally observed shift to the higher energy of the MLCT transition in solvents of high polarity has been attributed to the ground state stabilization or the excited state destabilization of non-centrosymmetric complexes in more polar solvents. Furthermore strong solvatochromism is expected when the dissolved complex is ionic/polar.

The mononuclear and binuclear cationic complexes of 4-cyanopyridine also exhibited broad medium intensity bands centred around 360 nm and 350 nm respectively. This band is assigned to metal to ligand charge transfer transition from Ru(II) to the antibonding C_5H_5 orbitals. The possibility of these bands arising from other MLCT transitions may be ruled out since the likelihood of transitions appearing from Ru(II) to either EPh_3 ($E = P, As$) or dppe/dppm in the near u.v. region is obscure. The intra-ligand $\pi \rightarrow \pi^*$ transitions in 4-CNpy lie in the region < 300 nm

(ca, 250–256 nm). These bands did not show any solvatochromic effect in the 4-CNpy complexes indicating no change in the dipole moments of the molecule in the ground and excited states.

In mononuclear and binuclear 4-CNpy 1-oxide complexes there appeared to be a very weak band in the visible region 400–500 nm, assigned to metal to ligand charge transfer band. Since this band is very weak and it appears to be masked by the tail of the 350 nm band, no solvatochromic effect could be studied. A band in the region (340–370 nm) was found to be very slightly solvent sensitive, showing a little solvatochromic effect. These bands have been assigned to either $n-\pi^*$ transition where one of the p-electrons is excited from the non-bonding orbital of the oxygen atom to an antibonding π^* orbital or to the MLCT (Ru(II) to antibonding C_5H_5 orbitals). Very strong absorption bands appeared in the u.v. region < 300 nm (Fig. IV.9), (λ_{max} varies within a range 280–300 nm depending on the solvent used) in the spectra of both the mononuclear and the binuclear 4-CNpy 1-oxide complexes. These strong bands due to a $\pi \rightarrow \pi^*$ charge transfer in the pyridine oxide ring, were found to be the most striking feature in these complexes,^{44,45} and are very sensitive to nature of the solvents used. This suggested a strong interaction between the NO group and the π -electrons of the ring. These transitions also showed a distinct blue shift in going from non polar to polar solvents. In -OH group containing polar solvents like

methanol or isopropyl alcohol there is an average shift of (10-15 nm) in λ_{max} towards the higher energy side. Such hypsochromic shifts could be explained on the basis of stabilization of the ground state by hydrogen bonding between pyridine 1-oxide ring and methanol or isopropyl alcohol.

Cyclic voltammograms were recorded at $0.2 \text{ volt sec}^{-1}$ in acetonitrile and the values of $E_{1/2}$ (vs SSCE) for the different processes are shown in (Table IV.5) including corresponding values for related mononuclear and binuclear species. Both the metal and ligand centered redox processes were found to be chemically irreversible. For monodentate 4-CNpy complexes the Ru(III)/Ru(II) potentials fall within the range consistent with pyridine nitrogen coordination. The C_5H_5 and PPh_3 centred redox processes were also observed⁴⁶ $E_{1/2}$ (0.59V) besides the 4-cyanopyridine centred redox process.

Table IV.1(a) Preparation, analytical data and physical properties of the complexes

Sl. NO.	Ligands		Anion	Time (hr)	Colour (M.P./°C)	Found(calc.) %			I.R. band (CN) ⁻¹	¹ H NMR (C ₅ H ₅), δ ppm	¹³ C NMR (C ₅ H ₅), δ ppm	
	L	R				C	H	N				
1	2	3	4	5	6	7	8	9				
1.	P	P	4-CNPy	Cl	6	T (105)	68.2 (67.9)	4.41 (4.69)	3.1 (3.37)	2240	4.6 (s)	83.0, 84.5
2.	P	P	4-CNPy	BPh ₄	-	B (150)	75.8 (76.5)	5.2 (5.3)	2.7 (2.5)	2248	4.58(s)	83.2, 84.5
3.	P	P	4-CNPy	PF ₆	-	RB (158-160)	59.3 (60.1)	4.3 (4.15)	2.4 (3.0)	2245	4.6 (s)	83.59, 84.9
4.	A	A	4-CNPy	Cl	8	T (94)	62.1 (61.4)	4.6 (4.2)	2.9 (3.0)	2243	4.62(s)	83.0, 84.6
5.	A	A	4-CNPy	BPh ₄	-	B (155)	70.7 (70.9)	5.1 (4.9)	2.4 (2.3)	2243	4.58(s)	83.6, 84.6
6.	A	A	4-CNPy	PF ₆	-	RB (164-166)	53.8 (54.9)	4.0 (3.8)	3.1 (2.7)	2245	4.6 (s)	83.2, 84.0
7.	A	P	4-CNPy	Cl	6	T (100)	64.9 (64.5)	4.9 (4.5)	2.9 (3.2)	2242	4.6 (s)	83.4, 84.8
8.	A	P	4-CNPy	BPh ₄	-	B (153)	74.0 (73.6)	5.5 (5.1)	2.8 (2.4)	2243	4.64(s)	83.0, 84.2
9.	A	P	4-CNPy	PF ₆	-	RB (160)	56.9 (57.4)	4.3 (3.9)	2.2 (2.8)	2242	4.6 (s)	83.5, 84.5
10.	dppe		4-CNpy	Cl	10	Y (130)	62.8 (63.1)	4.8 (4.7)	3.89 (3.97)	2243	4.98(s)	81.0, 82.5
11.	dppe		4-CNpy	BPh ₄	-	B (164)	74.8 (74.2)	5.7 (5.4)	3.1 (2.8)	2245	4.8 (s)	81.0, 82.4

...contd.

Table IV.1(a) (contd.)

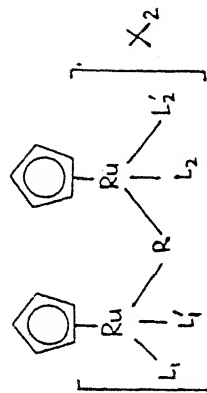
1	2	3	4	5	6	7	8	9			
12.	dppe	4-CNpy	PF ₆	-	YB (165)	53.9 (54.6)	4.06 (4.05)	3.1 (3.4)	2244	4.92 (s)	81.4, 82.6
13.	dppm	4-CNpy	Cl	12	Y (135)	63.1 (62.6)	4.2 (4.5)	3.9 (4.1)	2245	4.9 (s)	81.0, 81.9
14.	dppm	4-CNpy	BPh ₄	-	B (158)	54.8 (54.0)	3.9 (3.8)	3.2 (3.5)	2243	4.9 (s)	81.5, 82.9
15.	dppm	4-CNpy	PF ₆	-	YB (160)	74.6 (73.9)	5.4 (5.24)	2.6 (2.9)	2242	4.86 (s)	81.5, 82.5
16.	P	4-CNpyo	Cl	5	Y (120)	66.8 (66.6)	3.94 (4.6)	3.8 (3.3)	2238, 1295	4.6 (s)	84.0 (s)
17.	P	4-CNpyo	BPh ₄	-	Y (140)	74.8 (75.4)	5.59 (5.2)	2.78 (2.48)	2240, 1298	4.6 (s)	84.3 (s)
18.	P	4-CNpyo	PF ₆	-	Y (148)	58.8 (59.0)	4.3 (4.1)	2.7 (2.93)	2238, 1290	4.65 (s)	83.9 (s)
19.	A	4-CNpyo	Cl	5	Y (115-120)	63.8	4.5	3.7	2237, 1310	4.6 (s)	83.3 (s)
20.	A	4-CNpyo	BPh ₄	-	Y (130)	73.0 (72.6)	5.3 (5.0)	2.5 (2.38)	2240, 1300	4.5 (s)	84.0
21.	A	4-CNpyo	PF ₆	-	Y (145)	56.9 (56.4)	3.3 (3.9)	2.5 (2.8)	2238, 1295	4.6 (s)	84.5
22.	A	4-CNpyo	Cl	5	Y (125)	61.0 (60.3)	4.4 (4.2)	3.1 (2.9)	2240, 1300	4.7 (s)	83.5 (s)
23.	A	4-CNpyo	BPh ₄	-	Y (128)	69.3 (70.0)	5.2 (4.8)	2.5 (2.3)	2236, 1305	4.68 (s)	83.8 (s)
24.	A	4-CNpyo	PF ₆	-	Y (143)	54.5 (54.0)	4.2 (3.7)	3.2 (2.7)	2237, 1298	4.6 (s)	84.0 (s)
25.	dppe	4-CNpyo	Cl	6	Y (125-130)	62.1 (61.6)	4.9 (4.6)	4.2 (3.8)	2236, 1305	4.9 (s)	83.17 (s)

...contd.

Table IV.1(a) (contd.)

1	2	3	4	5	6	7	8	9			
26.	dppe	4-CNpyo	BPh ₄	-	Y (152)	73.4 (72.9)	5.5 (5.3)	3.0 (2.8)	2238,1298	4.96(s)	83.2(s)
27.	dppe	4-CNpyo	PF ₆	-	Y (150)	54.0 (53.5)	4.3 (3.9)	3.6 (3.3)	2239,1305	4.92(s)	83.4(s)
28.	dppm	4-CNpyo	Cl	6	Y (132)	61.8 (61.2)	4.9 (4.4)	4.2 (3.9)	2242,1295	4.9(s)	83.0(s)
29.	dppm	4-CNpyo	BPh ₄	-	Y (148)	72.2 (72.6)	5.6 (5.2)	3.0 (2.8)	2238,1300	4.84(s)	83.6(s)
30.	dppm	4-CNpyo	PF ₆	-	Y (145)	53.8 (53.0)	4.2 (3.8)	3.8 (3.4)	2239,1305	4.86(s)	83.2(s)

Table IV.1(b)



Sl. No.	Ligands			X ⁻ Anion	Colour (m.p./°C)	Found (calc.) %			I.R. band (CN) (cm ⁻¹)	¹ H NMR (δ ppm) C ₅ H ₅	¹³ C NMR (δ ppm) C ₅ H ₅
1	L ₁	L ₁ '	L ₂	L ₂ '	R	C	H	N	6	7	8
31.	P	P	P	P	4-CP	76.2 (76.9)	5.4 (5.37)	1.2 (1.3)	2238	4.3, 4.75	83.0, 84.5
32.	P	P	P	P	4-CP	60.2 (59.5)	4.4 (4.17)	1.62 (1.57)	2236	4.3, 4.8	83.2, 84.4
33.	P	P	A	A	4-CP	74.6 (73.8)	5.5 (5.2)	1.6 (1.26)	2237	4.2, 4.7	83.3, 84.8

...contd.

Table IV.1(b) (contd.)

1	2		3	4	5		6	7	8				
34.	P	P	A	A	4-CP	PF ₆	OB (168)	56.9 (56.7)	4.2 (3.9)	1.8 (1.5)	2236	4.28, 4.7	83.5, 84.5
35.	A	P	A	P	4-CP	PF ₆	B (165)	57.0 (56.7)	4.3 (3.9)	1.7 (1.5)	2235	4.3, 4.8	83.0, 84.4
36.	A	A	A	A	4-CP	BPh ₄	M (155)	70.7 (71.0)	4.3 (4.9)	1.53 (1.2)	2235	4.3, 4.68	82.9, 84.0
37.	A	A	A	A	4-CP	PF ₆	OB (168-170)	54.7 (54.1)	4.1 (3.8)	1.7 (1.4)	2237	4.4, 4.8	83.0, 84.5
38.		dppe	P	P	4-CP	BPh ₄	M (142-145)	75.2 (75.7)	5.5 (5.4)	1.6 (1.4)	2238	4.34, 4.7	81.9, 82.6
39.		dppe	A	A	4-CP	BPh ₄	M (140)	72.9 (72.5)	5.8 (5.2)	1.6 (1.3)	2240	4.4, 4.74	82.0, 82.9
40.		dppe		dppe	4-CP	BPh ₄	M (148)	71.1 (71.6)	5.7 (5.3)	1.8 (1.4)	2238	4.4, 4.69	81.3, 82.7
41.		dppm	P	P	4-CP	BPh ₄	M (145)	74.5 (75.6)	5.4 (5.34)	1.28 (1.4)	2237	4.3, 4.7	81.3, 82.2
42.		dppm	A	A	4-CP	BPh ₄	B (138)	72.9 (72.5)	5.8 (5.2)	1.6 (1.3)	2240	4.4, 4.6	80.8, 82.7
43.		dppm		dppm	4-CP	PF ₆	B (135-140)	51.2 (50.6)	4.2 (3.7)	2.3 (1.8)	2238	4.3, 4.5	81.2, 82.5
44.	P	P	P	P	4-CNpyo	BPh ₄	YB (148)	76.9 (76.3)	5.7 (5.3)	1.6 (1.3)	2230, 1294	4.7(s)br	83.4, 84.2
45.	P	P	P	P	4-CNpyo	PF ₆	Y (130-132)	58.3 (58.9)	4.6 (4.1)	1.8 (1.56)	2232, 1295	4.62(s)br	83.9, 84.5
46.	A	P	A	P	4-CNpyo	PF ₆	Y (142)	56.8 (56.2)	4.4 (3.9)	1.9 (1.5)	2230, 1290	4.7(s)br	83.4, 84.2

...contd.

Table IV.1(b) (contd.)

1	2	3	4	5	6	7	8				
47.	A A A	4-CNpyo	PF ₆	YB (145)	54.0 (53.7)	3.9 (3.7)	1.78 (1.4)	2234, 1295	4.68(s)br	84.0, 84.8	
48.	P A A	4-CNpyo	PF ₆	YB (145-148)	56.8 (56.2)	4.3 (3.9)	1.8 (1.5)	2236, 1292	4.7(s)br	83.8, 84.6	
49.	dppe	dppe	4-CNpyo	PF ₆	Y (155)	45.9 (45.2)	3.9 (3.4)	2.4 (1.8)	2232, 1290	4.9(s)br	81.9, 82.3
50.	dppm	dppm	4-CNpyo	PF ₆	YB (152)	44.9 (44.5)	3.8 (3.2)	2.2 (1.9)	2234, 1295	4.86(s)	82.0, 83.6

P = PPh₃; A = AsPh₃; dppe = 1,2 Bis(diphenylphosphinoethane); dppm = 1,2 Bis(diphenylphosphinomethane);

4-CNpy = 4-cyanopyridine; 4-CNpyo = 4-cyanopyridineoxide; T = Tan; B = Brown; RB = Reddish brown;

Y = Yellow; YB = Yellowish brown; M = Maroon; OB = Orangish brown.

Table IV.2. Equivalent Conductivity Data of the Complexes

Compound	$c \times 10^4$ eq/lit	$\sqrt{c} \times 10^2$	λ_e ohm ⁻¹ cm ² eq ⁻¹	λ_o ohm ⁻¹ cm ² eq ⁻¹	$\lambda_o - \lambda_e$
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(4\text{-CNpy})(\text{PPh}_3)_2]\text{PF}_6$	7.56	2.75	117.8		7.2
	12.96	3.60	117.0		8.0
	18.06	4.25	114.9	125	10.1
	22.09	4.70	113.9		11.1
	39.69	6.30	112.1		12.9
	57.76	7.60	109.8		15.2
$[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-4-CNpy})-(\text{PPh}_3)_4](\text{PF}_6)_2$	0.56	0.75	170.2		4.8
	4.41	2.10	165.8		9.2
	7.29	2.7	162.8		12.2
	12.96	3.6	157.0	175	18.0
	21.16	4.6	150.9		24.1
	39.69	6.3	139.5		35.5
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(4\text{-CNpyO})(\text{PPh}_3)_2]\text{PF}_6$	2.89	1.7	143.2		6.8
	8.41	2.9	139.9		10.1
	11.9	3.45	137.5	150	12.5
	20.25	4.5	133.8		16.2
	29.37	5.42	132.0		18.1
	42.45	6.5	127.5		22.5
$[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-4-CNpyO})-(\text{PPh}_3)_4](\text{PF}_6)_2$	0.77	0.88	205.5		7.0
	4.0	2.0	199.0		13.5
	7.34	2.71	192.0	212.5	20.5
	10.24	3.2	189.3		23.2
	15.36	3.92	183.5		29.0
	27.04	5.2	177.4		35.1

Table IV.3a. Electronic Spectral Data of the Complexes in Various Solvents

Solvents	Complexes λ_{\max} (nm); log ϵ			
	A	B	C	D
Acetone	470; 3.671	-	-	-
Acetonitrile	460; 3.528	455; 3.790	291.6; 3.934 350 ; 3.976	295; 4.439 353; 4.121
Chloroform	-	-	297 ; 3.819 362 ; 4.127	299; 4.568 364; 4.384
Dichloromethane	483; 3.722	450; 3.826	297 ; 3.849	296; 4.322 363;
Dimethylformamide	490; 3.584	480; 3.728	295 ; 3.778 347 ; 3.814	297; 4.356 355; 4.045
Dimethylsulphoxide	-	-	299 ; 3.753 355 ; 3.784	295; 4.322 355; 4.124
Isopropyl alcohol	-	-	287.5; 3.856 356 ; 3.817	289; 4.505 365; 4.146
Methanol	465; 3.184	470; 4.041	289 ; 4.021 354 ; 4.394	287; 4.492 358; 4.133
Nitromethane	430; 3.586	420; 3.465	-	-
Propylene carbonate	475; 3.676	475; 3.856	294 ; 3.762 347 ; 3.778	298; 4.137 354; 4.029

Table IV.3b. Solvent Parameters

Solvents	D_s	D_{op}	$\frac{1}{D_{op}} - \frac{1}{D_s}$	E_T	DN	E_{MLCT}^*
Dichloromethane	8.9	2.028	0.38	41.1	-	0.67
Chloroform	4.7	2.085	0.267	-	-	0.42
Acetone	20.7	1.84	0.495	42.2	17.0	0.82
Acetonitrile	36.2	0.53	0.53	46.0	14.1	0.98
Dimethylformamide	36.7	2.046	0.461	43.8	26.6	0.95
Dimethylsulfoxide	49.0	2.18	0.438	45.0	29.8	1.00
Methanol	32.6	1.76	0.537	55.5	19.0	0.73
Nitromethane	38.6	1.91	0.498	46.3	-	-
Nitrobenzene	34.8	2.40	0.388	42.0	-	-
Propylene Carbonate	65.1	0.48	0.48	46.6	15.1	-

Table IV.4. Values for Ruthenium(II) 4-cyanopyridine and
 Ruthenium(II) 4-cyanopyridine 1-oxide complexes
 vs. SSCE at $22 \pm 2^\circ\text{C}$ in acetonitrile

Complexes	Process	$E_{1/2}$ (volts)
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(4\text{-CNpy})(\text{PPh}_3)_2]\text{Cl}$	$\text{Ru}^{\text{III}}/\text{II}$	0.52, 1.24
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}4\text{-CNpy})(\text{PPh}_3)_4](\text{BPh}_4)_2$	$\text{Ru}^{\text{III}}/\text{II}$	0.26, 0.96
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(4\text{-CNpy})(\text{PPh}_3)_2]\text{Cl}$	$\text{Ru}^{\text{III}}/\text{II}$	0.8 , 1.16
$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}4\text{-CNpyo})(\text{PPh}_3)_4](\text{PF}_6)_2$	$\text{Ru}^{\text{III}}/\text{II}$	0.36, 1.12

List of Figures

Fig. IV.1. Conductivity Plots of the Complexes

- (a) Plots of $\lambda_o - \lambda_e$ vs \sqrt{c}
- (b) Plots of λ_e vs \sqrt{c} for the complexes
 - o $[(\eta^5-C_5H_5)Ru(4-CNpy)(PPh_3)_2]PF_6$
 - x $[(\eta^5-C_5H_5)_2Ru_2(\mu-4-CNpy)(PPh_3)_4](PF_6)_2$
 - Δ $[(\eta^5-C_5H_5)Ru(4-CNpyo)(PPh_3)_2]PF_6$
 - o $[(\eta^5-C_5H_5)_2Ru_2(\mu-4-CNpyo)(PPh_3)_4](PF_6)_2$

Fig. IV.2. Infra red Spectra of the Complexes

- (a) $[(\eta^5-C_5H_5)Ru(4-CNpy)(PPh_3)_2]BPh_4$
- (b) $[(\eta^5-C_5H_5)Ru(4-CNpy)dppe]Cl$
- (c) $[(\eta^5-C_5H_5)_2Ru_2(\mu-4-CNpy)(AsPh_3)_4](BPh_4)_2$

- Fig. IV.3. (a) $[(\eta^5-C_5H_5)Ru(4-CNpyo)(PPh_3)_2]PF_6$
 (b) $[(\eta^5-C_5H_5)Ru(4-CNpyo)(AsPh_3)_2]BPh_4$

Fig. IV.4. 1H NMR Spectra of the Complexes

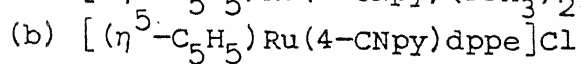
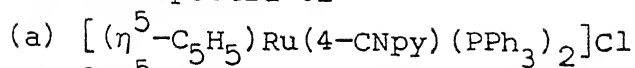
- (a) $[(\eta^5-C_5H_5)_2Ru_2(\mu-4-CNpy)(PPh_3)_4](PF_6)_2$
- (b) $[(\eta^5-C_5H_5)Ru(4-CNpyo)(PPh_3)_2]Cl$
- (c) $[(\eta^5-C_5H_5)Ru(4-CNpyo)dppe]Cl$
- (d) $[(\eta^5-C_5H_5)Ru(4-CNpy)(PPh_3)_2]PF_6$

Fig. IV.5. ^{13}C NMR Spectra of the Complexes

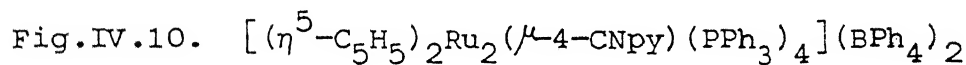
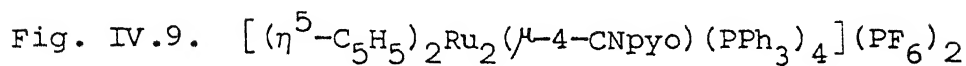
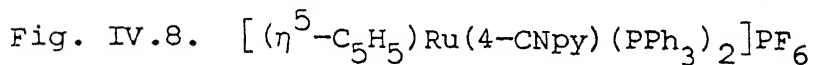
- (a) $[(\eta^5-C_5H_5)Ru(4-CNpy)(PPh_3)_2]PF_6$
- (b) $[(\eta^5-C_5H_5)Ru(4-CNpyo)(PPh_3)_2]Cl$
- (c) $[(\eta^5-C_5H_5)Ru(4-CNpy)(dppe)]Cl$
- (d) $[(\eta^5-C_5H_5)Ru(4-CNpyo)(dppe)]Cl$

- Fig. IV.6. (a) $[(\eta^5-C_5H_5)_2Ru_2(\mu-4-CNpy)(PPh_3)_4](BPh_4)_2$
 (b) $[(\eta^5-C_5H_5)_2Ru_2(dppm)(PPh_3)_4(\mu-4-CNpyo)](BPh_4)_2$

Fig. IV.7. ^{31}P NMR Spectra of



Electronic Spectra of the Complexes



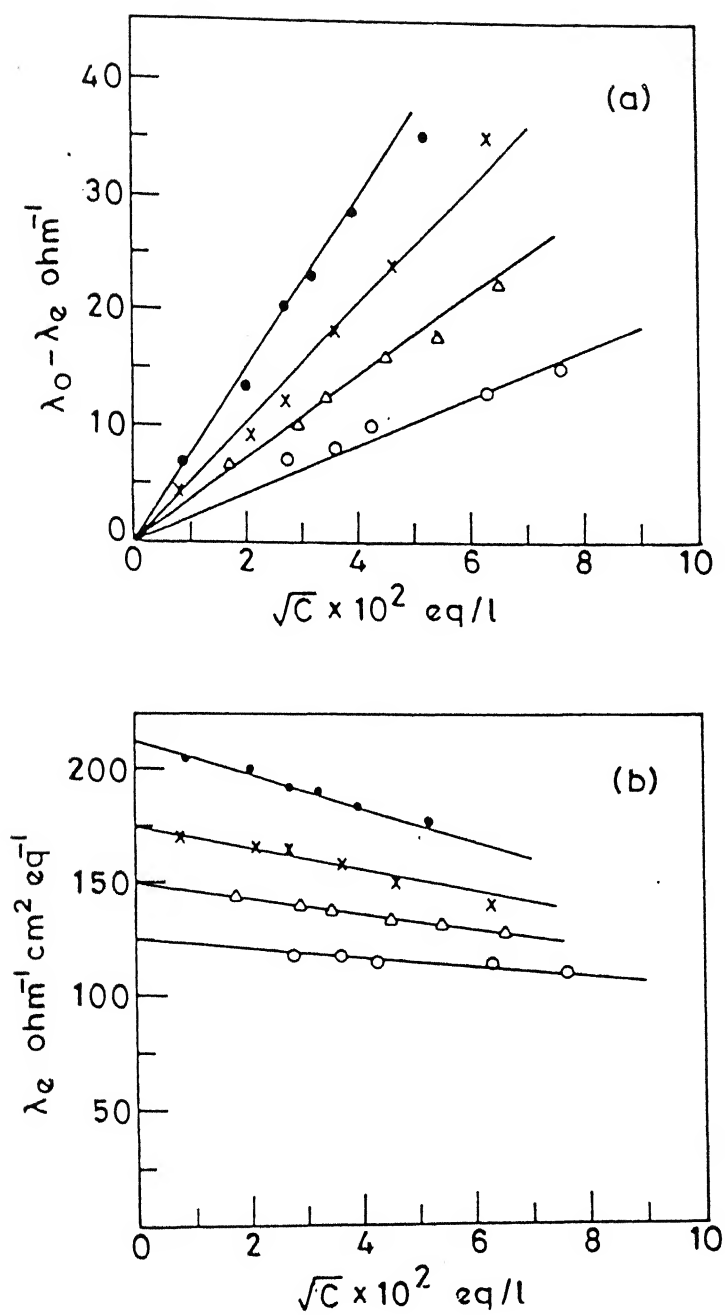


Fig.IV.1

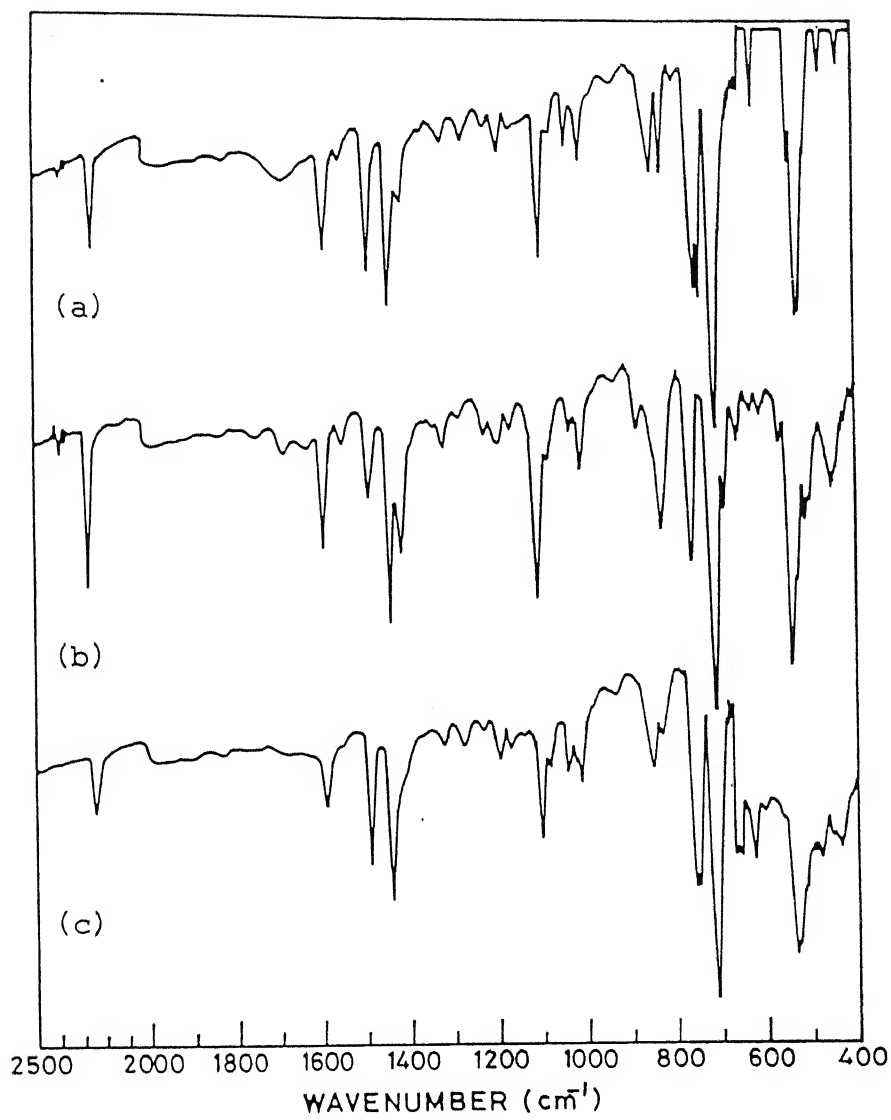


Fig. IV.2

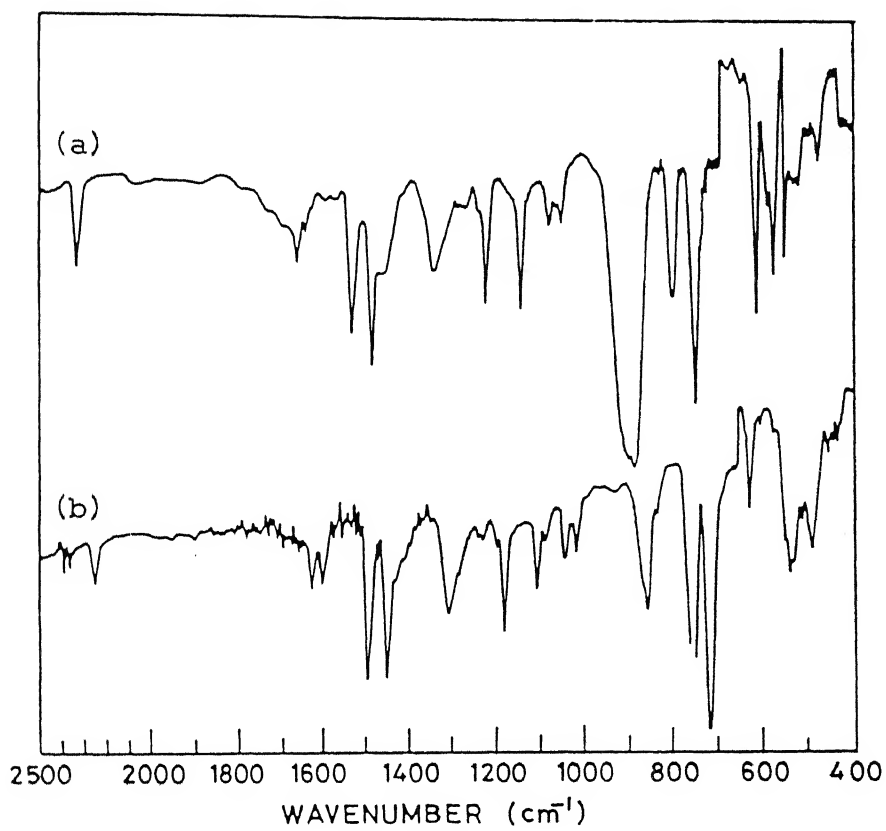


Fig.IV.3

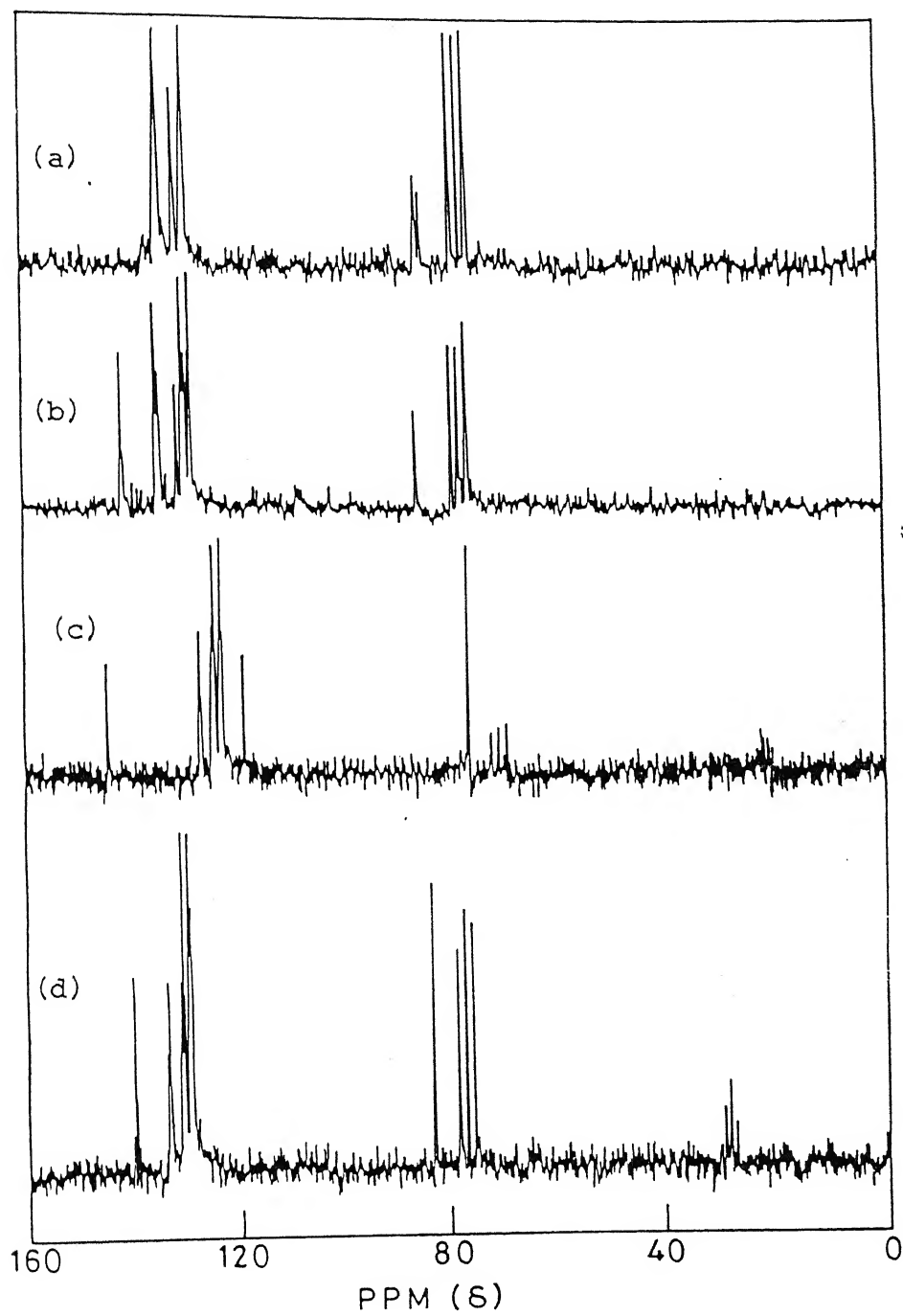


Fig.IV.5

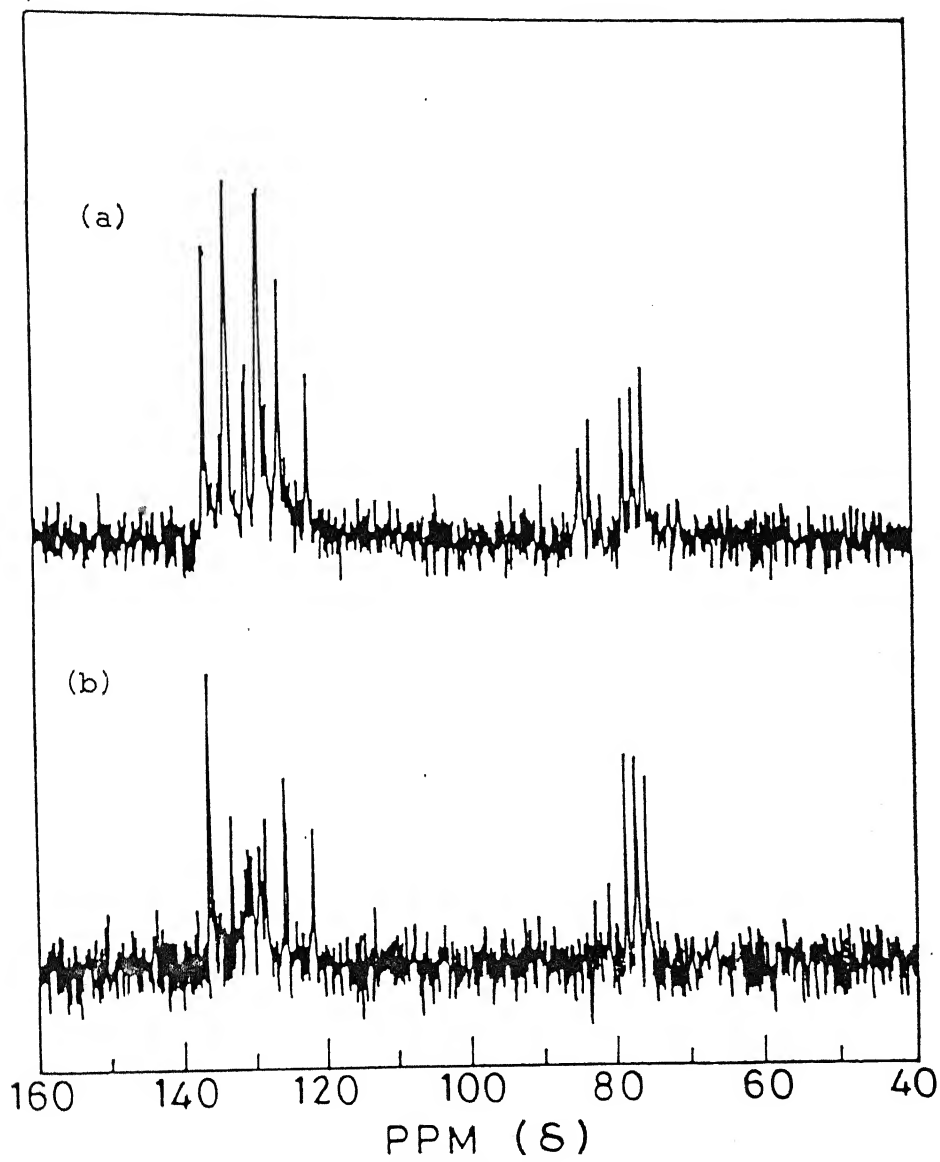


Fig.IV. 6

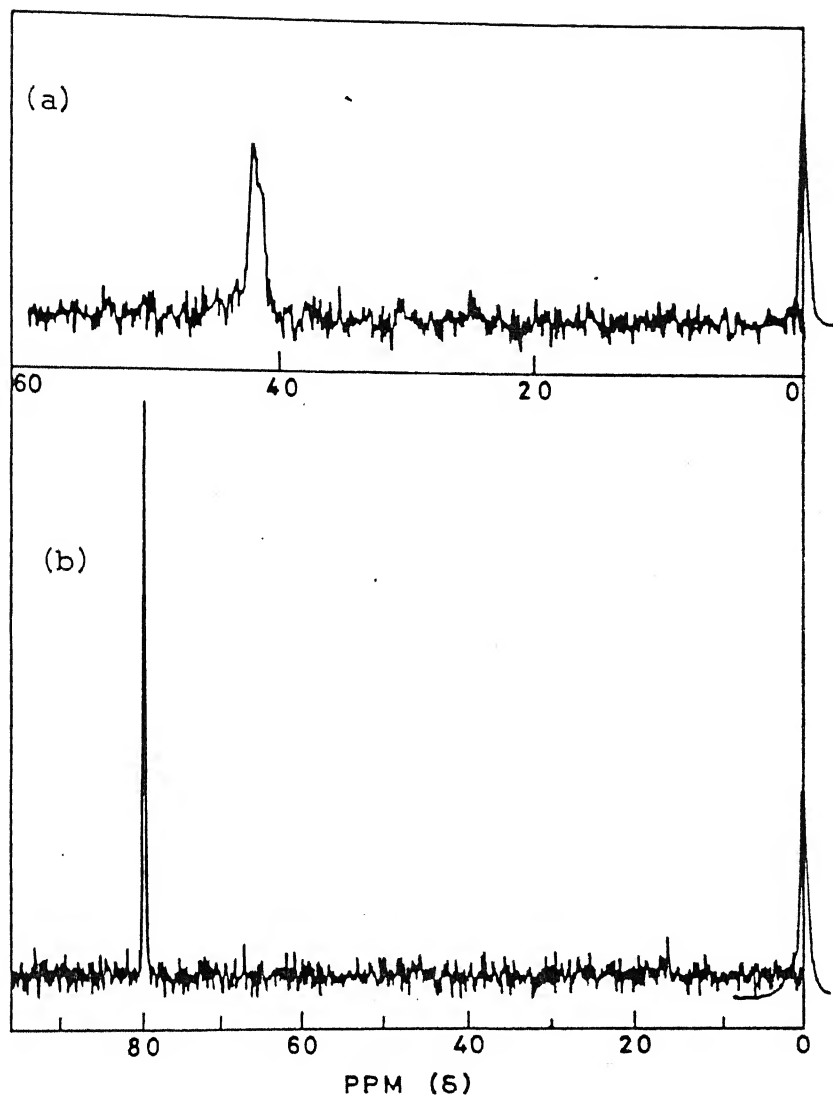


Fig.IV.7

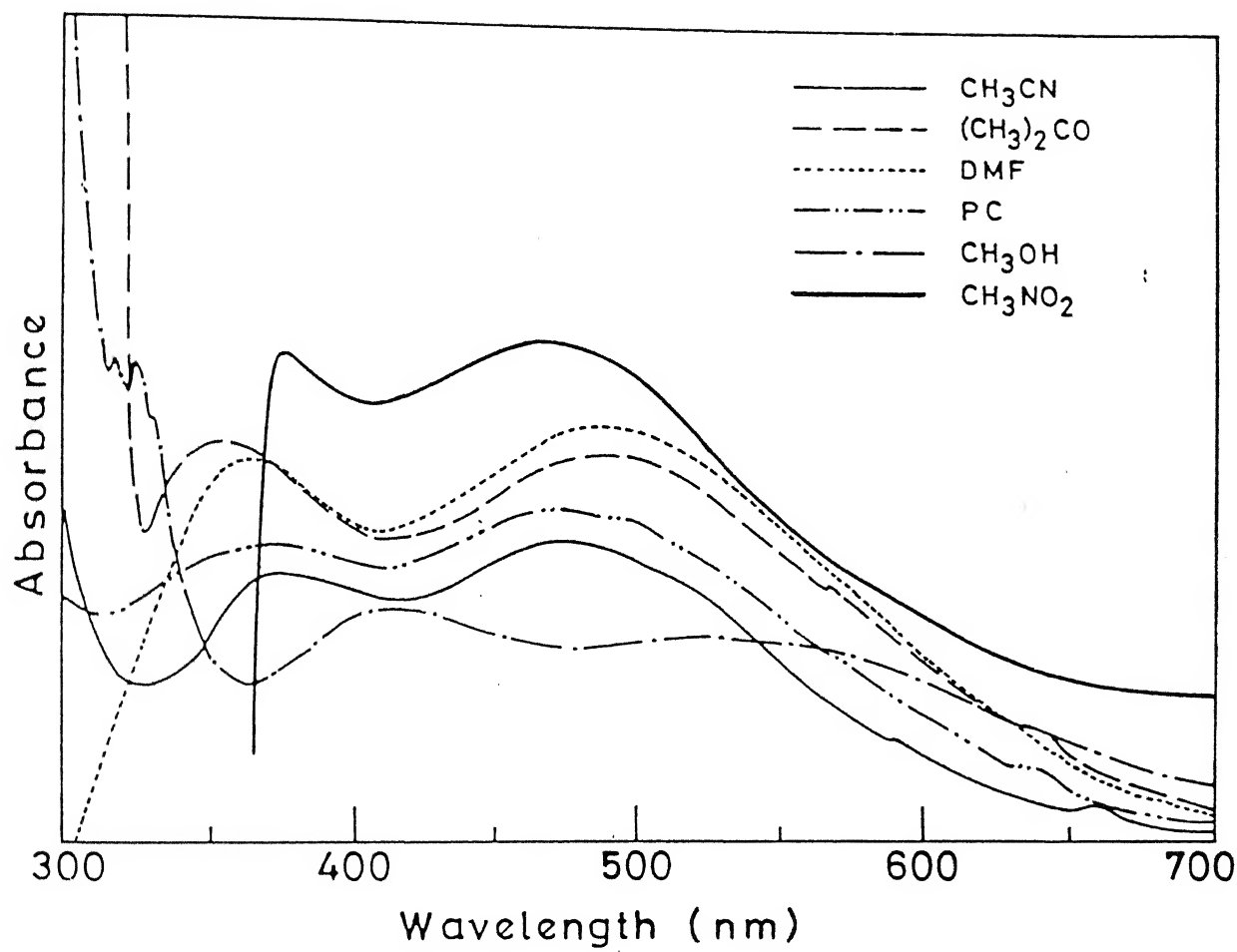


Fig.IV.8

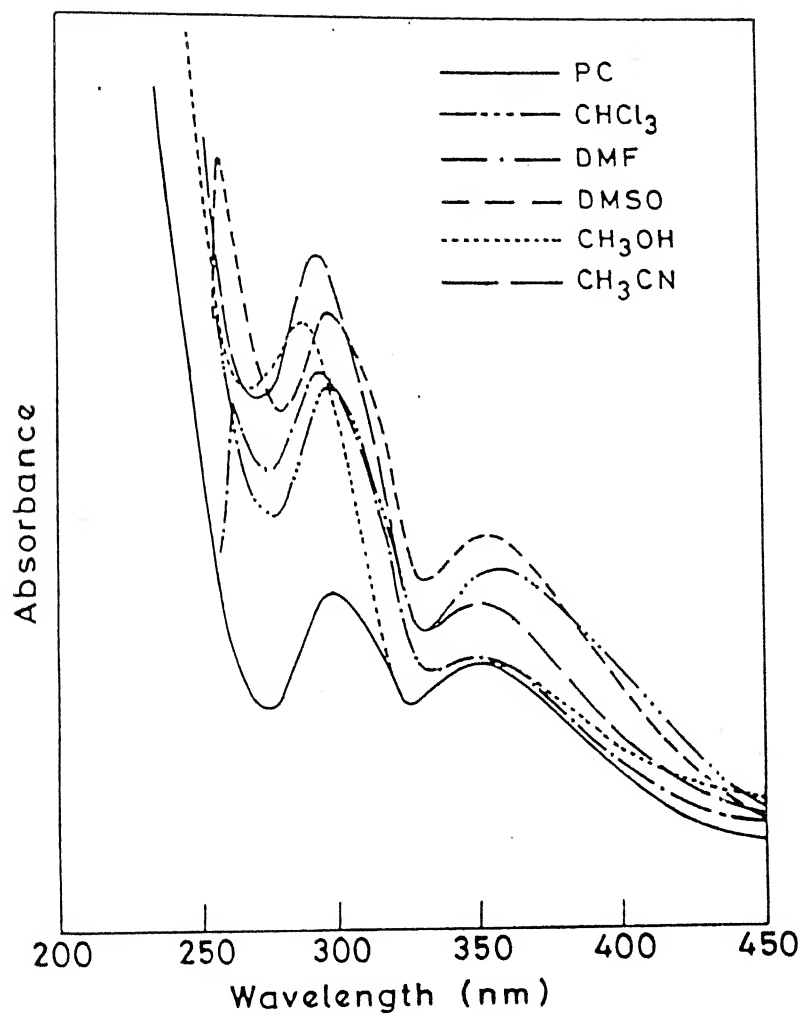


Fig.IV.9

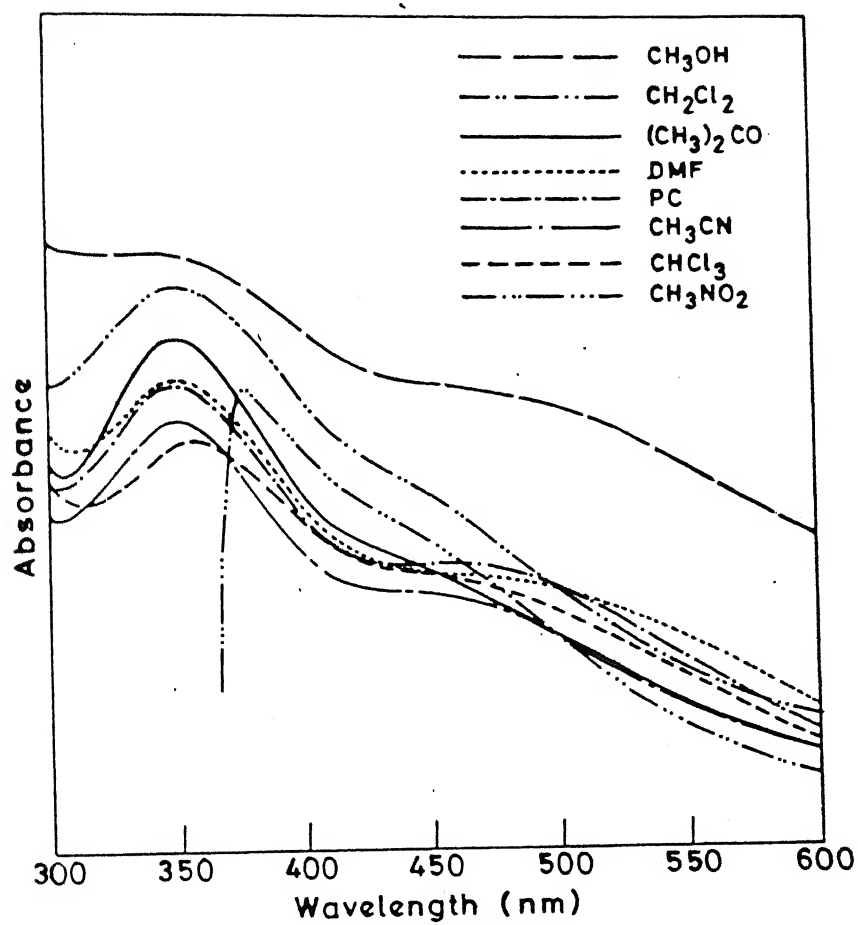


Fig.IV.10

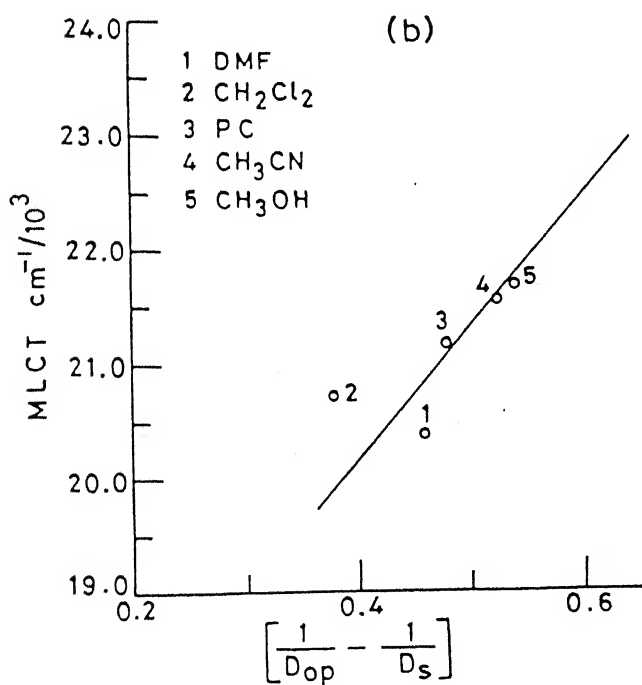
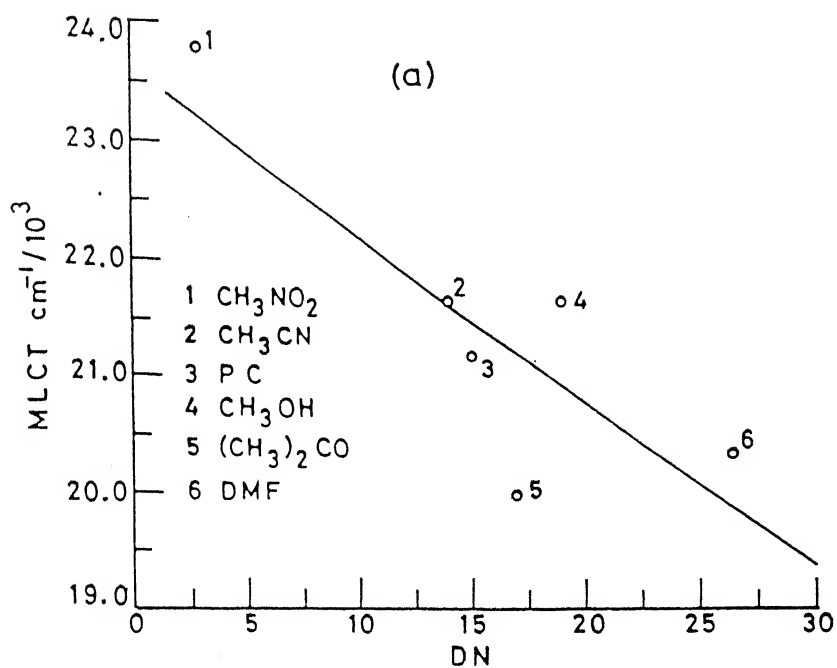


Fig.IV.11. (a) Plot of D_N vs $\nu(\text{MLCT})$ for $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(4\text{-CNpy})-(\text{PPh}_3)_2]\text{BPh}_4$

(b) Plot of $[1/D_{\text{op}} - 1/D_s]$ vs $\nu(\text{MLCT})$ for $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(4\text{-CNpy})(\text{PPh}_3)_2]\text{BPh}_4$

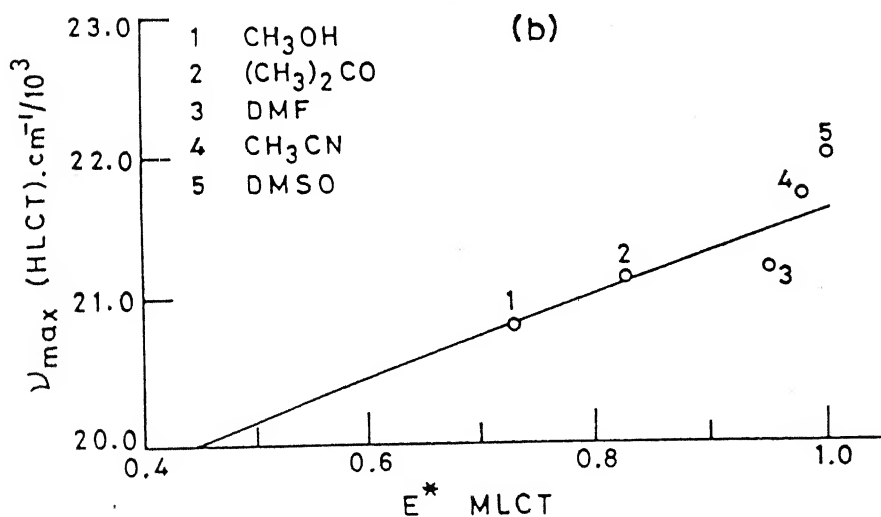
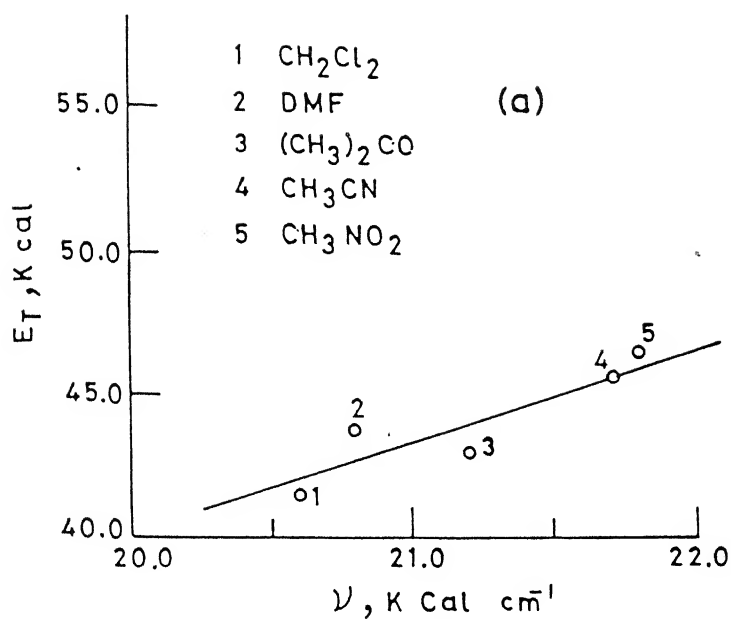


Fig. IV.12. (a) Plot of E_T vs $\nu(\text{MLCT})$ for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2^-(\mu\text{-4-CNpy})(\text{PPh}_3)_4](\text{BPh}_4)_2$

(b) Plot of E^*_{MLCT} vs $\nu(\text{MLCT})$ for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2^-(\mu\text{-4-CNpy})(\text{PPh}_3)_4](\text{BPh}_4)_2$

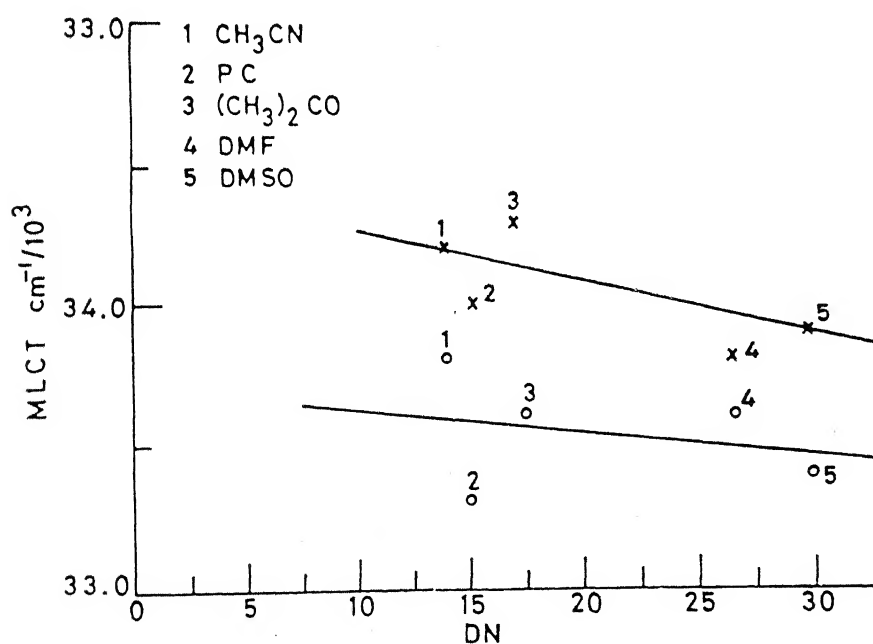
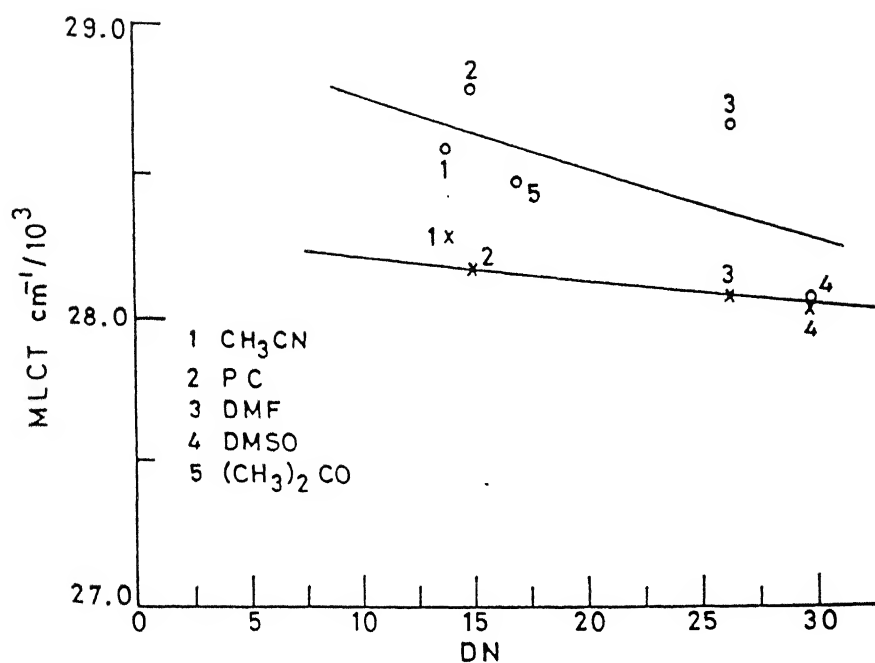


Fig.IV.13. Plots of DN vs $\nu(\text{MLCT})$ for
 o $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(4\text{-CNpyo})(\text{PPh}_3)_2]\text{PF}_6$
 x $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(4\text{-CNpyo})(\text{PPh}_3)_4](\text{PF}_6)_2$

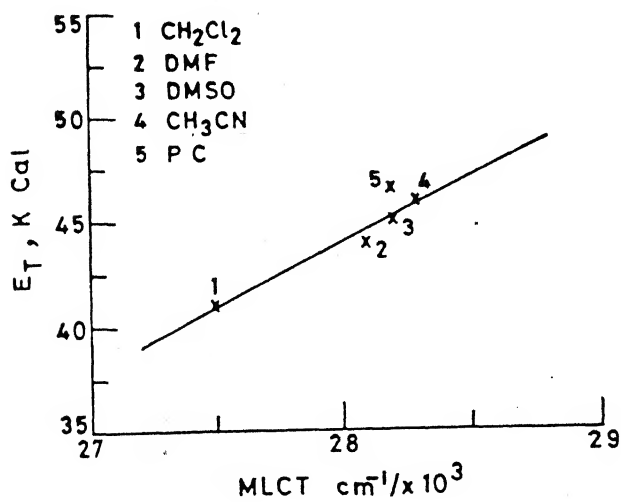
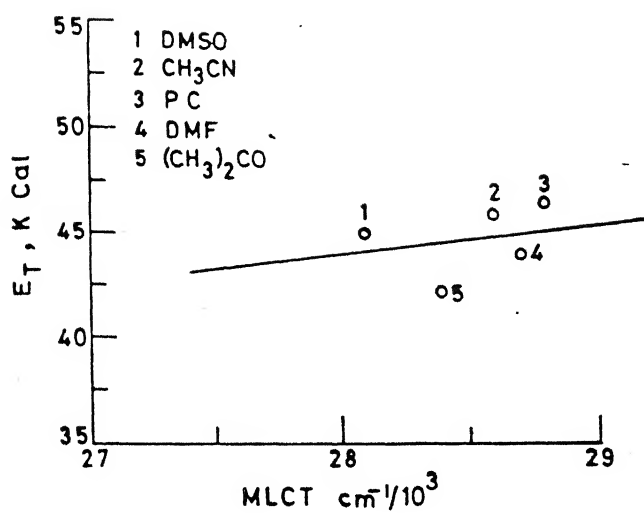
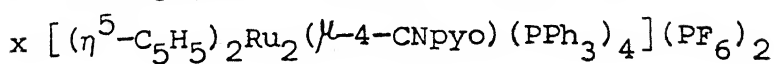
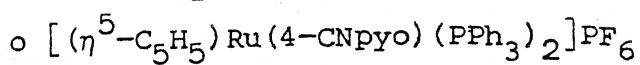


Fig.IV.14. Plots of E_T vs $\nu(\text{MLCT})$ for



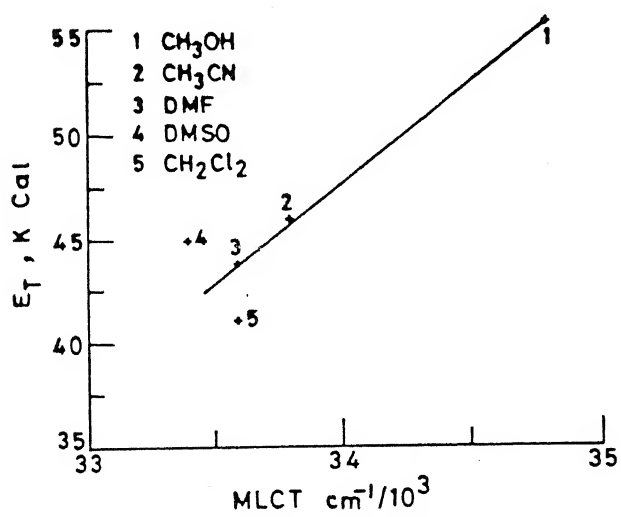
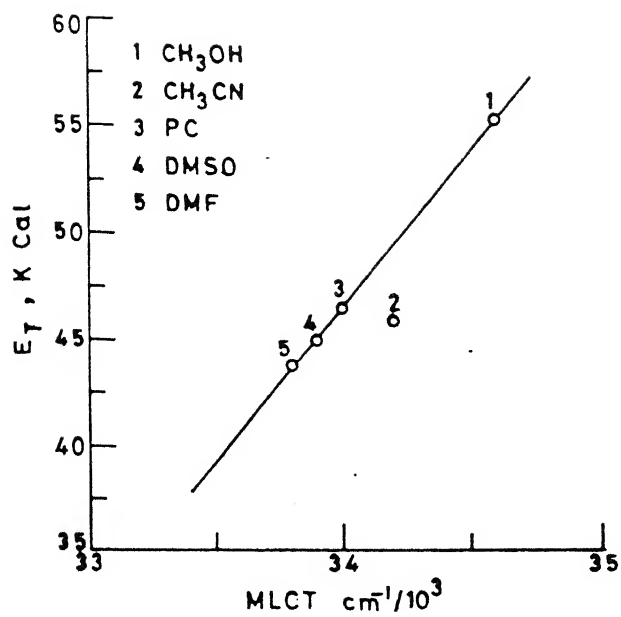
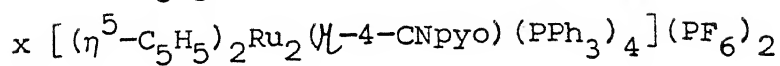
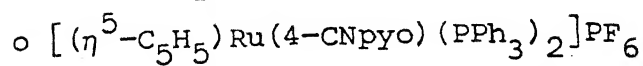


Fig.IV.15. Plots of E_T vs $\nu(\text{MLCT})$ for



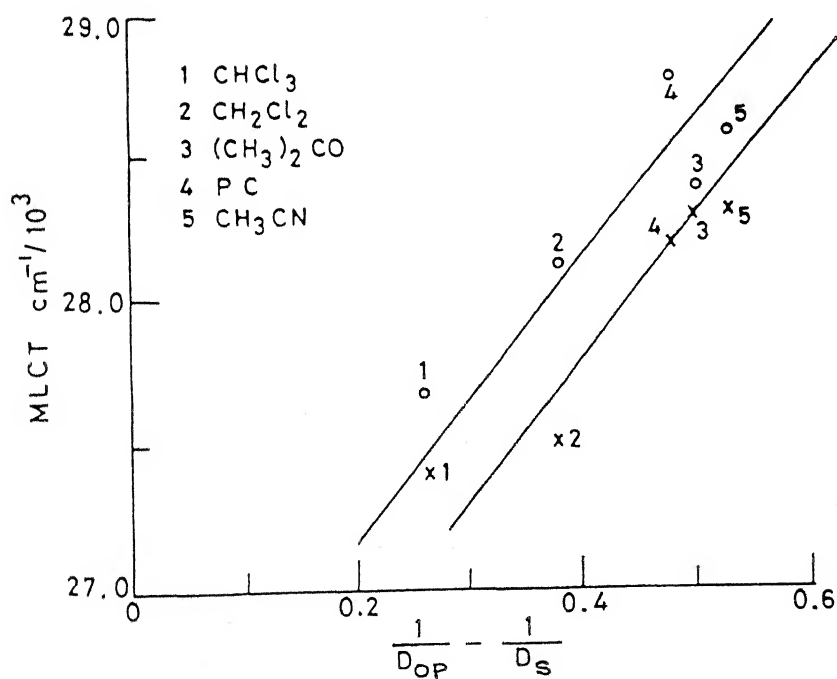
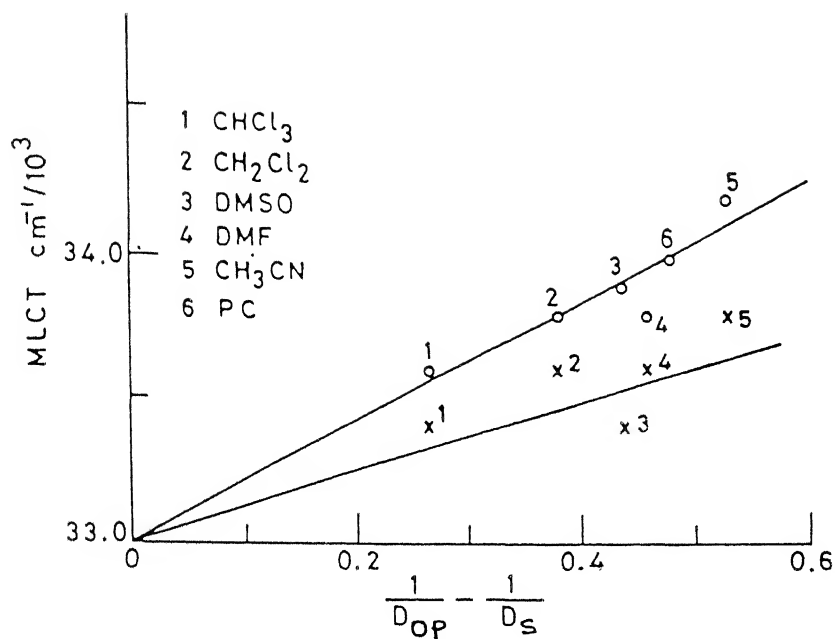


Fig. IV.16. Plots of $1/D_{OP} - 1/D_S$ vs $\nu(\text{MLCT})$ for
 o $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-4-CNpyo})(\text{PPh}_3)_4](\text{PF}_6)_2$
 x $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(4\text{-CNpyo})(\text{PPh}_3)_2]\text{Cl}$

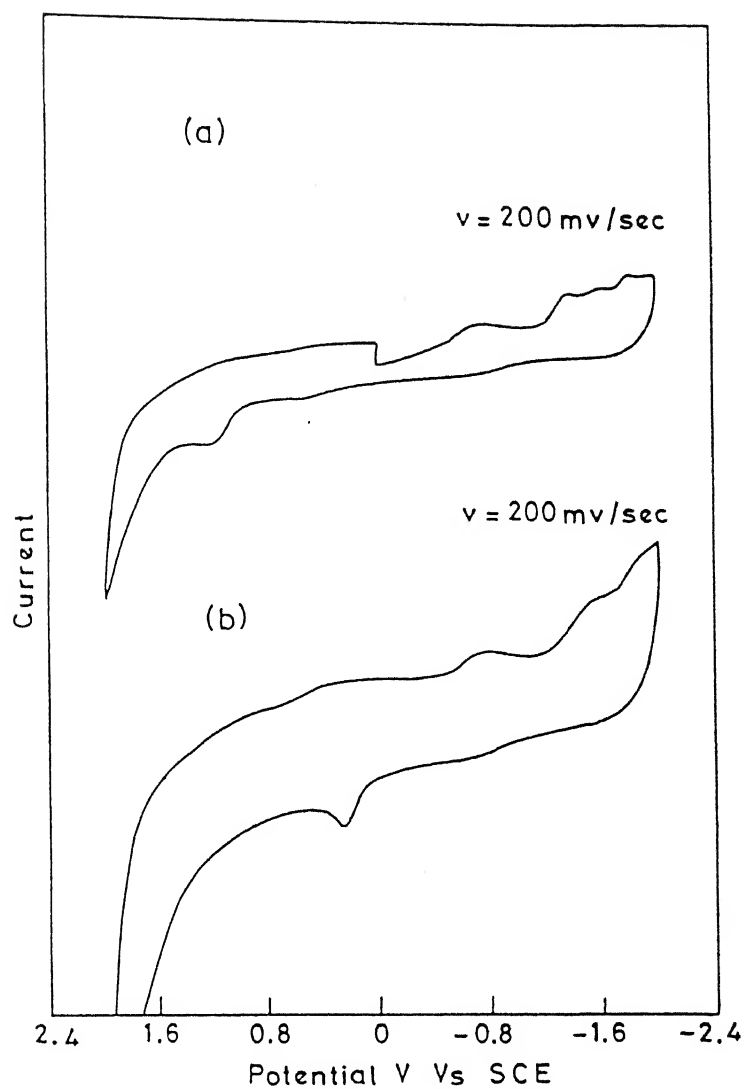
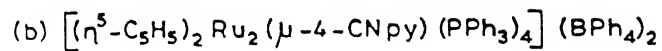
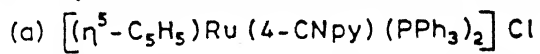


Fig.IV.17 Cyclic voltammogram of the complexes.



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Chapter V

REACTIONS OF 1,4-PIPERAZINEDICARBONITRILE AND 1-PIPERIDINE CARBONITRILE WITH η^5 -CYCLOPENTA- DIENYL RUTHENIUM(II) COMPLEXES

Introduction

A number of structures containing cyanamide (NH_2CN) having the two nitrogen atoms situated in significantly different electronic environments and thus making their nucleophilicity different have been proposed.¹⁻¹⁵ No definite structural decision regarding the nature of the orbital (sp^3 or p_z) containing the lone pair of electrons on the amino nitrogen has yet been arrived at conclusively. Although a variety of synthetic organic reactions involving cyanamide and carbodiimide nitrogen as a nucleophile have been reported,¹⁶⁻¹⁸ very little work has been carried out so far with regard to electrophilic attack of metal ions/complexes on the terminal electron-rich nitrogens. There is a likelihood of many of these reactions being nitrogen nucleophilicity dependent. In addition, the presence of a tautomeric equilibrium between the amide (major) and di-imide (minor) forms of cyanamide might complicate the reaction products.^{3-8,19,20}

Over the past few years we have been interested in studying the nucleophilic character of the nitrogen of metal-bonded cyano groups and wished to exploit this nucleophilicity in synthesising bridged metal complexes.²¹⁻²⁴ In this chapter we report the results obtained from the reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-ClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$; $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) or $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)] with 1,4-piperazinedicarbonitrile or 1-piperidinecarbonitrile.

Experimental

All chemicals were AnalaR grade and used without further purification. Solvents were dried before use.²⁵ The complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$) were prepared by the literature methods.²⁶⁻²⁹ Analytical and spectral data of the products were obtained as described elsewhere.²⁷ The electronic spectra (200–700 nm) of the complexes in chloroform solution were recorded on a Shimadzu U.V. 190 spectrophotometer. The ^{13}C n.m.r. spectra were obtained on a JEOL FT-90 spectrophotometer. Conductivity measurements were carried out in dry methanol using an Elico conductivity bridge type CM82T.

- (a) Reaction of 1,4-Piperazinedicarbonitrile with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-ClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$) in the presence of a suitable anion

A typical reaction procedure was as follows. The complex

$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ (0.13 mmol) was suspended in dry methanol (25 cm^3) containing a salt of a suitable anion (NH_4PF_6 , NaBF_4 , NaBPh_4 , or LiClO_4) (0.25 mmol) and 1,4-piperazinedicarbonitrile (0.14 mmol). The contents of the flask were refluxed for ca. 1 h whereby $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ started to dissolve slowly and bright yellow shining crystals of a complex appeared. These were separated by centrifugation. Further crystals were obtained by slow concentration of the centrifugate on a water-bath. The crystals were washed with methanol, diethyl ether, and light petroleum and dried under vacuum (yield, ca. 58 %). Analyses corresponded to the formula $[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{L}_2)_2(\mu\text{-C}_6\text{H}_8\text{N}_4)]\text{X}_2$ ($\text{L} = \text{PPh}_3$, AsPh_3 , or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X} = \text{PF}_6$, BF_4 , BPh_4 , or ClO_4).

(b) Reaction of 1-Piperidinecarbonitrile with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$
($\text{L} = \text{PPh}_3$, AsPh_3 , or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) in the
presence of a suitable anion

A typical reaction procedure was as follows. A suspension of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ (0.13 mmol), a salt of a suitable anion (NH_4PF_6 , NaBF_4 , NaBPh_4 , or LiClO_4) (0.25 mmol), and 1-piperidinecarbonitrile (0.18 mmol) was taken in dry methanol (25 cm^3). The resulting suspension was heated to reflux for ca. 2-3 h, whereupon the suspension dissolved to give a bright yellow solution. The resulting solution was concentrated slowly on a water-bath to nearly 5 cm^3 whereby yellow crystals separated out. These were

separated by centrifugation, washed with methanol, diethyl ether, and petroleum ether and dried under vacuum (yield, ca. 50 %). Analyses corresponded to the formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{-(C}_6\text{H}_{10}\text{N}_2)]\text{X}$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$; $\text{X} = \text{PF}_6^-, \text{BF}_4^-, \text{BPh}_4^-, \text{or ClO}_4^-$).

Results and Discussion

Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$) with 1,4-piperazinedicarbonitrile or 1-piperidinedicarbonitrile in the presence of a suitable anion (PF_6^- , BF_4^- , BPh_4^- , or ClO_4^-) yield bright yellow cationic binuclear and mononuclear complexes respectively. Microanalytical data suggested the formula given in the (Table V.1). They are non-hygroscopic, slightly soluble in methanol, chloroform, dichloromethane, acetone, benzene, and other halogenated organic solvents and insoluble in light petroleum or diethyl ether.

Conductivity Measurements

The distinction between the charges on the cationic species has also been confirmed by their conductivity measurements in highly pure and dry methanol, according to a procedure adopted by Feltham and Hayter.³⁰ They emphasized the need to carry out conductance measurements over a concentration range in order to distinguish between mononuclear and polynuclear species. From

the values of the equivalent conductance (λ_e) in the concentration range $10^{-2} - 10^{-4}$ equiv. l^{-1} , the equivalent conductance at zero concentration (λ_o) was determined by extrapolation (Figure V.1a) and subsequently values of $\lambda_o - \lambda_e$ [Figure V.1b] were plotted as a function of \sqrt{c} .³¹⁻³³ The slopes of these straight lines for the 1-piperidinecarbonitrile (271) and 1,4-piperazinedicarbonitrile (607) complexes compared very well with Feltham's values for 1:1 and 1:2 complexes, 288 and 552 respectively,^{34,35} providing further evidence regarding the charges on the cations. The bonding modes in the complexes and their tentative structures have been deduced following spectral studies.

I.R. Spectra

The model considered for the interpretation of the i.r. spectra of the complexes is assumed to be N,N-disubstituted nitrile ($>N-C\equiv N$). The possibility of the ligands existing in the carbodi-imide form ($-N=C=N-$) does not exist except for the contribution of a resonating structure where the lone pair on the $>N$ -nitrogen participates in a delocalisation process with separation of the charges ($>N^+=C=N^-$).¹⁻³ This will have some contribution only when the lone pair is present in the pure p_z orbital. According to the $>N-C\equiv N$ model, the i.r. spectra of 1-piperidinecarbonitrile, with C_s symmetry, should exhibit i.r.-active bands due to $\nu(C\equiv N)$, $\nu(C-N)$, and $\delta(NCN)$ around 2200, 1000, and 400 cm^{-1} respectively.¹ Presuming the carbodi-imide model

the vibrational spectra should differ because of the difference in the position of $\nu_{\text{sym}}(\text{N}=\text{C}=\text{N})$ and two NCN bending modes. The values of the fundamental mode frequencies and the force constants of $\nu(\text{N}-\text{C}\equiv\text{N})$ and $\nu(\text{N}=\text{C}=\text{N})$ should undoubtedly be similar, but if the two CN modes of $\nu(\text{N}=\text{C}=\text{N})$ are equivalent, a slightly lower value of $\nu_{\text{asym}}(\text{N}-\text{CN})$ (2070 cm^{-1}) than that of $\nu(\text{C}=\text{N})$ may be expected and the intensity of the symmetric stretching mode in $\text{N}=\text{C}=\text{N}$ should be much smaller.^{1,36} In the spectrum of 1-piperidinecarbonitrile two intense bands were found at 2240 and 1010 cm^{-1} and a weak broad band, at 430 cm^{-1} , attributable to $\nu(\text{C}\equiv\text{N})$, $\nu(\text{C}-\text{N})$, and $\delta(\text{NCN})$ respectively; the $\nu(\text{C}-\text{N})$ band at 1010 cm^{-1} is single and very sharp suggesting it to be unaffected by the 'neighbour interaction'.² In addition, there is a distinct splitting of $\nu(\text{C}\equiv\text{N})$ (not present in the spectra of the complexes), which may be because of the Fermi resonance between $\nu(\text{C}\equiv\text{N})$ and the overtone frequency involving the $\nu(\text{C}-\text{N})$ stretch. It is also likely that the non-involvement of the lone pair in resonance structure of $>\text{N}-\text{C}\equiv\text{N}$ may be related to the molecular non-planarity³ because of which the non-bonding orbital located at $>\text{N}$ -of the $>\text{N}-\text{C}\equiv\text{N}$ moiety instead of being in a pure p_z orbital, also has some s character and thus inhibits the contribution of $>\text{N}^+=\text{C}=\text{N}^-$ to the structure.

The i.r. spectra of the complexes of 1-piperidinecarbonitrile show bands at 2285 (single), 1010 and 430 cm^{-1} respectively.

The shift of the band at 2240 cm^{-1} to 2285 cm^{-1} implies direct co-ordination of ruthenium to the nitrogen of the $\text{C}\equiv\text{N}$ group. Furthermore the shift also indicates the absence of π -back-bonding from ruthenium and co-ordination through the triple bond of the CN group, which would cause a shift towards lower wavenumbers. The position of $\nu(\text{C-N})$ at 1010 cm^{-1} remained the same suggesting no effect on the >N-C bond order by co-ordination and implying non-involvement of the amide nitrogen lone pair in metal co-ordination. The i.r. spectra of 1,4-piperazinedicarbonitrile and its complexes are, as expected similar to those of 1-piperidinecarbonitrile and its complexes (Figure V.2). The two $\text{>N-C}\equiv\text{N}$ groups, being too far separated, do not interact to cause either broadening or splitting of the $\nu(\text{N-C}\equiv\text{N})$ bands. Unfortunately we are unable to assign conclusively $\nu(\text{Ru-N})$ because of the presence of a number of bands in the lower wavenumber region. Nonetheless a band at 430 cm^{-1} has tentatively been assigned to $\nu(\text{Ru-N})$. This band does not exist in the free ligand spectra.

Electronic Spectra

The electronic spectra of the mono- and bi-nuclear complexes show a broad medium intensity band centred around 360 nm (Table V.1) which we assign to a metal to ligand charge-transfer

(MLCT) transition (Ru^{II} to the anti-bonding C_5H_5 orbitals). The possibility of this band arising from other MLCT. transitions may be ruled out since the likelihood of transitions appearing from Ru^{II} to either EPh_3 or the antibonding $\text{C}\equiv\text{N}$ orbitals in the near u.v. region ($\lambda = 350 \text{ nm}$) is obscure.³⁷ The band at 360 nm did not show any solvatochromic effect indicating no change in the dipole moments of the molecule in the ground and excited states; this further supports our assignment because the presence of a ruthenium to 1-piperidinecarbonitrile or 1,4-piperazinedicarbonitrile charge-transfer band would change the dipole moment of the excited states.

Bands present in the 200-330 nm region were impossible to assign due to the extensive overlapping of a number of intraligand and other m.l.c.t. bands.³⁷ The complexes did not exhibit any bands in the visible region.

N.M.R. Spectra

^1H n.m.r. spectra of the 1,4-piperazinedicarbonitrile complexes exhibited peaks around δ 7.2-7.5 (EPh_3), 4.65 ($\eta^5\text{-C}_5\text{H}_5$), and 3.1 (CH_2 protons of the piperazine ring). In the spectra of the 1-piperidinecarbonitrile complexes peaks appeared around δ 7.4-7.7 (EPh_3 , $\text{E} = \text{P, As, or Sb}$), 4.7 ($\eta^5\text{-C}_5\text{H}_5$), and 3.25, 1.95, and 1.8 (CH_2 protons of piperidine ring) (Figure V.3).

The positions of the C_5H_5 protons in the spectra of both complexes were comparable with those of $[Ru(\eta^5-C_5H_5)(EPh_3)(CN)]$ ($E = P, As, \text{ or } Sb$).³⁸ This suggests that the $>\ddot{N}-C\equiv N$ moiety affects the environment around the C_5H_5 protons in a similar manner to the $C\equiv N$ group. The nitrogen atom attached to $-C\equiv N$ in the $>\ddot{N}-C\equiv N$ moiety does not seem to have much effect on the C_5H_5 protons through their lone pair. This further supports the non-involvement of the nitrogen lone pair in the resonance possibly due to the molecular non-planarity (cf. i.r. spectra).

^{13}C n.m.r. spectra of the complexes showed that the carbon of $>\ddot{N}-C\equiv N$ resonates at around δ 137.7-138.7 p.p.m. and exhibits a distinct shift towards a lower field compared to that in 1-piperidinecarbonitrile or 1,4-piperazinedicarbonitrile (δ 117 p.p.m.) (Fig. V.4). This indicates deshielding of the carbon atom in the $>\ddot{N}-C\equiv N$ moiety on co-ordination. It could be that on complexation of nitrogen to ruthenium, the electron density on the carbon atom of the $-C\equiv N$ group is polarized towards nitrogen resulting in deshielding of the carbon nucleus. It is also noteworthy that if the amide nitrogen lone pair was involved in the resonance, the possibility of deshielding should have been much less, thus again supporting the non-planarity of the molecule.

Based on the above spectral, analytical, and conductivity data, it appears certain that the metal is co-ordinated through

the nitrogen of the CN group, however the molecules may have a number of conformers (chair, boat, cis-trans etc.).

The existence of the complexes of 1,4-piperazinedicarbonitrile in the boat form could be tentatively ruled out on the following grounds. (i) The steric interaction between the two NCN groups present in 1,4 positions will be very prominent making the boat form highly unstable and energetically unfavourable. (ii) Lone pair-lone pair repulsions on the two nitrogen atoms of the ring should make the boat form energetically less favourable compared to the chair form. Thus the chair form is preferred (see below) in which the nitrogens of the piperazine ring are far apart and the substituents in trans positions.

Similarly in the 1-piperidinecarbonitrile complexes the chair form is also preferred with the NCN substituent occupying an equatorial position to avoid steric interaction with the neighbouring CH_2 groups within the ring.

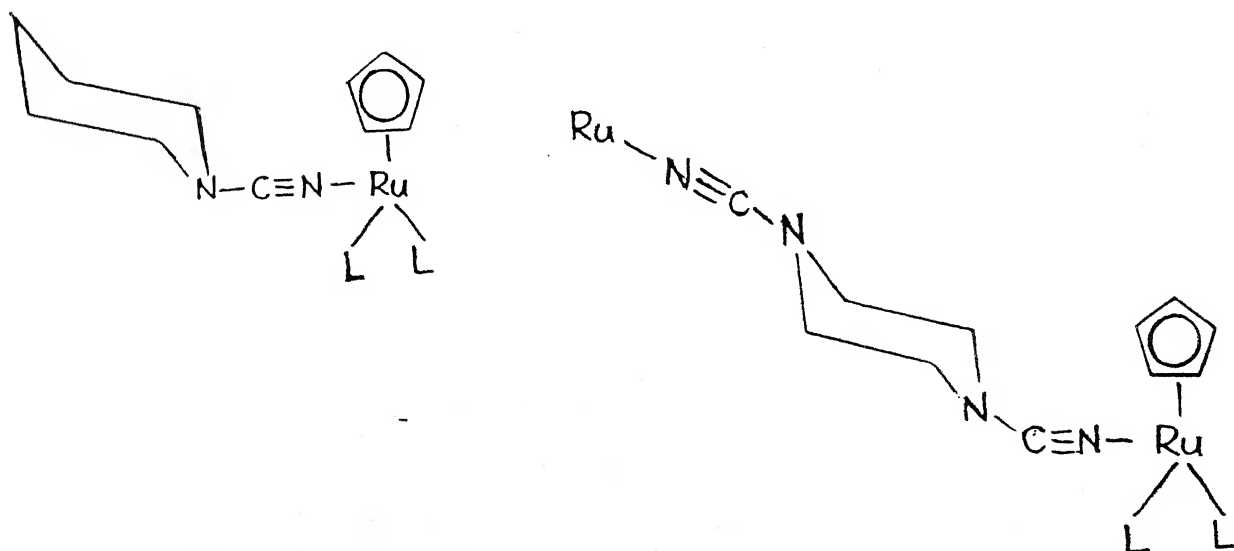


Table V.1. Characterization Data of the Complexes.

Sl. No.	Ligands			Anion	Analysis			U.V. spectra λ_{\max} , (log ϵ)	C_5H_5 ^1H NMR (δ ppm)	
	L_1 (Colour, m.p., $^\circ\text{C}$)	L_2	L_3		Found (calc.)	C	H	N		
1	2	3	4	5	6	7	8	9	10	11
1.	P P P P (Y, 165-170)	P	BF ₄	61.8 (62.4)	4.64 (4.6)	3.49 (3.3)				4.65
2.	P P P P (Y, 179)	P	PF ₆	58.1 (58.4)	4.36 (4.3)	2.91 (3.1)		358, (4.68)		4.7
3.	P P P P (Y, 165)	P	BPh ₄	74.9 (75.7)	5.2 (5.4)	2.42 (2.6)				4.6
4.	P P P P (Y, 167)	P	ClO ₄	-	-	-				-
5.	A P A P (Y, 175)	P	BF ₄	58.8 (59.3)	4.51 (4.38)	2.9 (3.1)				4.6
6.	A P A P (Y, 175-180)	P	PF ₆	56.5 (55.7)	4.23 (4.1)	2.54 (2.95)		361.5, (4.72)		4.65
7.	A P A P (Y, 157-160)	P	BPh ₄	72.64 (72.7)	6.0 (5.3)	2.8 (2.49)				4.7
8.	A P A P (Y, 169-171)	P	ClO ₄	-	-	-				-
9.	A A A A (Y, 179)	A	BF ₄	55.4 (56.6)	4.03 (4.2)	2.38 (3.0)				4.75
10.	A A A A (Y, 182)	A	PF ₆	54.03 (53.3)	4.3 (3.9)	2.83 (2.8)		360, (4.71)		4.7

...contd.

Table V.1(contd.)

1	2	3	4	5	6	
11.	A A A A (Y, 162-164)	BPh ₄	69.5 (70.0)	5.51 (5.06)	2.28 (2.4)	4.6
12.	A A A A (Y, 175)	ClO ₄	-	-	-	-
13.	Sb Sb Sb Sb (Y, 174)	BF ₄	52.18 (51.4)	4.83 (3.8)	2.15 (2.7)	4.5
14.	Sb Sb Sb Sb (Y, 193-195)	PF ₆	49.7 (48.6)	4.73 (3.59)	2.85 (2.58)	4.6
15.	Sb Sb Sb Sb (Y, 161)	BPh ₄	65.2 (64.8)	4.62 (4.98)	2.59 (2.34)	4.6
16.	Sb Sb Sb Sb (Y, 165)	ClO ₄	-	-	-	-
17.	DPPE DPPE (Y, 248)	BF ₄	56.2 (56.74)	4.83 (4.58)	3.6 (3.89)	4.8
18.	DPPE DPPE (Y, 252)	PF ₆	51.63 (52.4)	5.09 (4.2)	3.88 (3.5)	4.85
19.	DPPE DPPE (Y, 239)	BPh ₄	72.8 (73.18)	5.41 (5.57)	2.87 (2.94)	4.9
20.	DPPE DPPE (Y, 240)	ClO ₄	-	-	-	-
21.	DPPM DPPM (Y, 158)	BF ₄	55.8 (56.17)	4.5 (4.39)	3.42 (3.97)	4.8
22.	DPPM DPPM (Y, 162-164)	PF ₆	50.64 (51.6)	4.22 (4.05)	3.16 (3.6)	4.75

Table V.1 (contd.)

1	2		3	4		5	6
	DPPM (Y, 160)	DPPM		BPh ₄			
23.				73.4 (72.9)	5.89 (5.4)	2.73 (2.98)	4.8
24.	DPPM (Y, 164)	DPPM	ClO ₄	-	-	-	-
L ₁ L ₂							
25.	P (Y, 168)	P	BF ₄	62.9 (63.58)	5.32 (5.07)	2.98 (3.15)	4.6
26.	P (Y, 170-172)	P	PF ₆	60.7 (59.68)	4.96 (4.76)	2.88 (2.96)	4.7
27.	A (Y, 162)	P	BF ₄	61.1 (60.58)	4.3 (4.83)	2.67 (3.0)	4.65
28.	A (Y, 167)	P	PF ₆	57.6 (57.0)	4.98 (4.55)	2.32 (2.83)	4.6
29.	A (Y, 159)	A	BF ₄	58.2 (57.84)	4.45 (4.61)	2.61 (2.87)	4.7
30.	A (Y, 162-165)	A	PF ₆	55.21 (54.59)	5.0 (4.35)	2.65 (2.71)	4.6
31.	Sb (Y, 173)	Sb	BF ₄	52.03 (52.75)	4.68 (4.2)	2.5 (2.61)	4.6
32.	Sb (Y, 179)	Sb	PF ₆	49.8 (50.04)	3.7 (3.99)	2.15 (2.48)	4.65

...contd.

Table V.1(contd.)

1	2	3	4		5	6
33.	DPPE (Y, 240)	BF ₄	57.9 (58.3)	5.4 (5.1)	3.7 (3.67)	4.8
34.	DPPE (Y, 246)	PF ₆	53.8 (54.2)	4.32 (4.76)	3.1 (3.4)	4.8
35.	DPPM (Y, 162)	BF ₄	58.2 (57.8)	4.73 (4.9)	3.2 (3.74)	4.75
36.	DPPM (Y, 172-174)	PF ₆	54.0 (53.6)	4.82 (4.47)	3.24 (3.47)	4.8

Y = Yellow; P = PPh₃; A = AsPh₃; Sb = SbPh₃; DPPE = 1,2 Bis(diphenylphosphinoethane);

DPPM = 1,2 Bis(diphenylphosphinomethane).

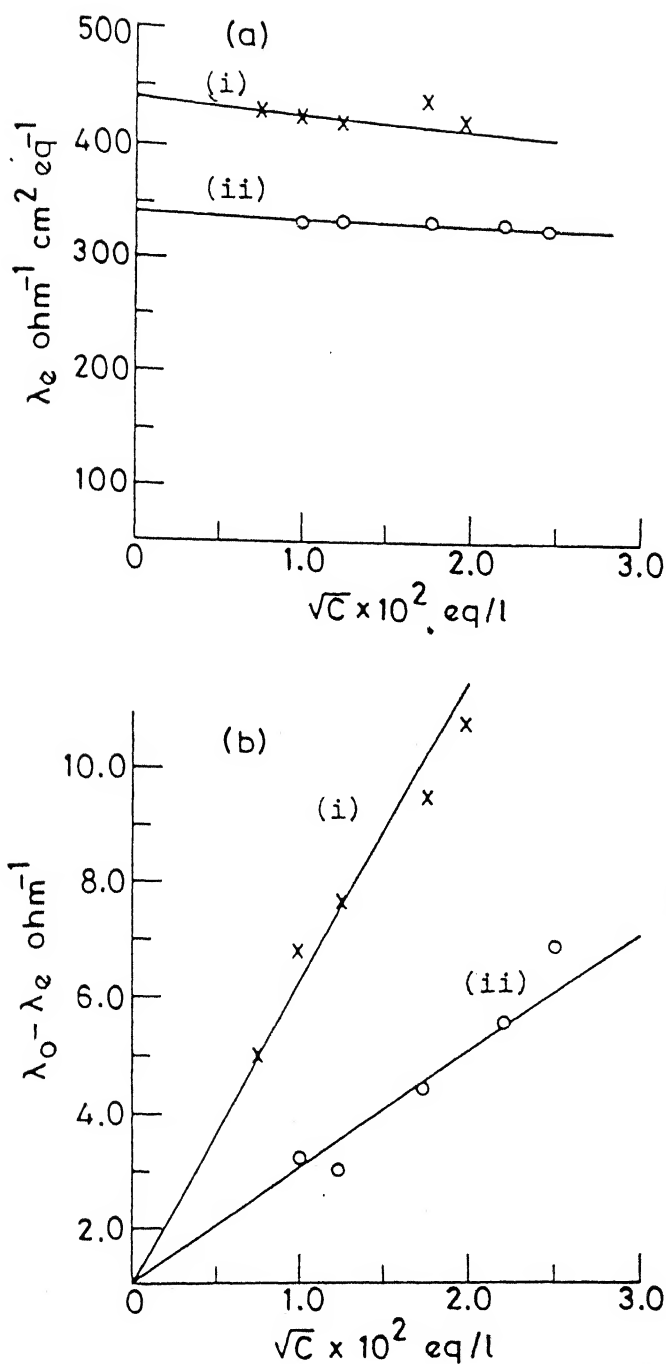


Fig.V.1. Plots of (a) equivalent conductance λ_e vs \sqrt{c} and (b) $(\lambda_o - \lambda_e)$ vs \sqrt{c} for (i) $[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)_4]^{2-}(\mu\text{-C}_6\text{H}_8\text{N}_4)](\text{PF}_6)_2$ and (ii) $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10}\text{N}_2)]\text{PF}_6$

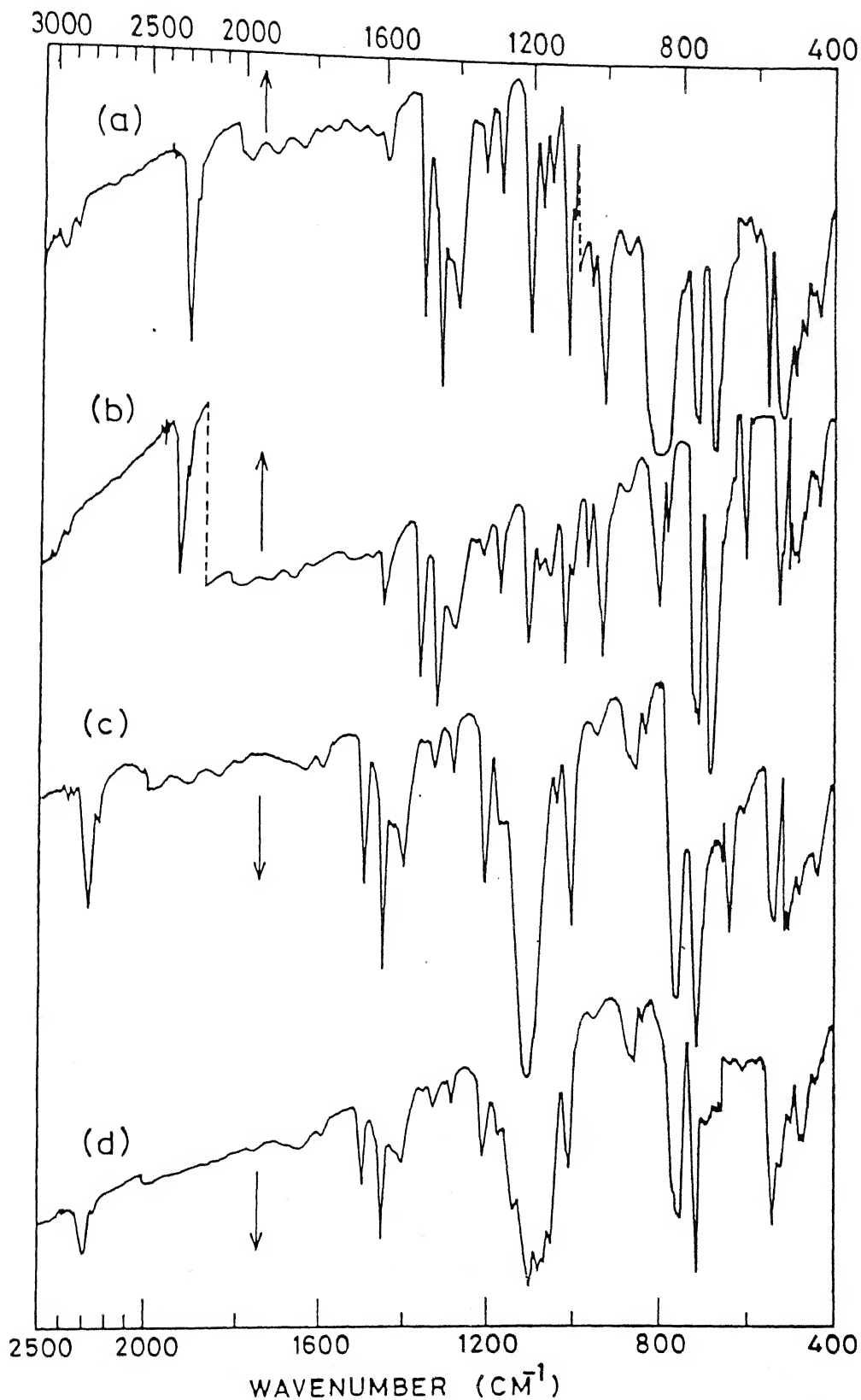


Fig.V.2. Infrared Spectra of (a) $[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)_4(\mu\text{-C}_6\text{H}_8\text{N}_4)](\text{PF}_6)_2$; (b) $[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{AsPh}_3)_4(\mu\text{-C}_6\text{H}_8\text{N}_4)](\text{BPh}_4)_2$; (c) $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{AsPh}_3)(\text{C}_6\text{H}_{10}\text{N}_2)]\text{ClO}_4$; (d) $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2(\text{C}_6\text{H}_{10}\text{N}_2)]\text{BF}_4$

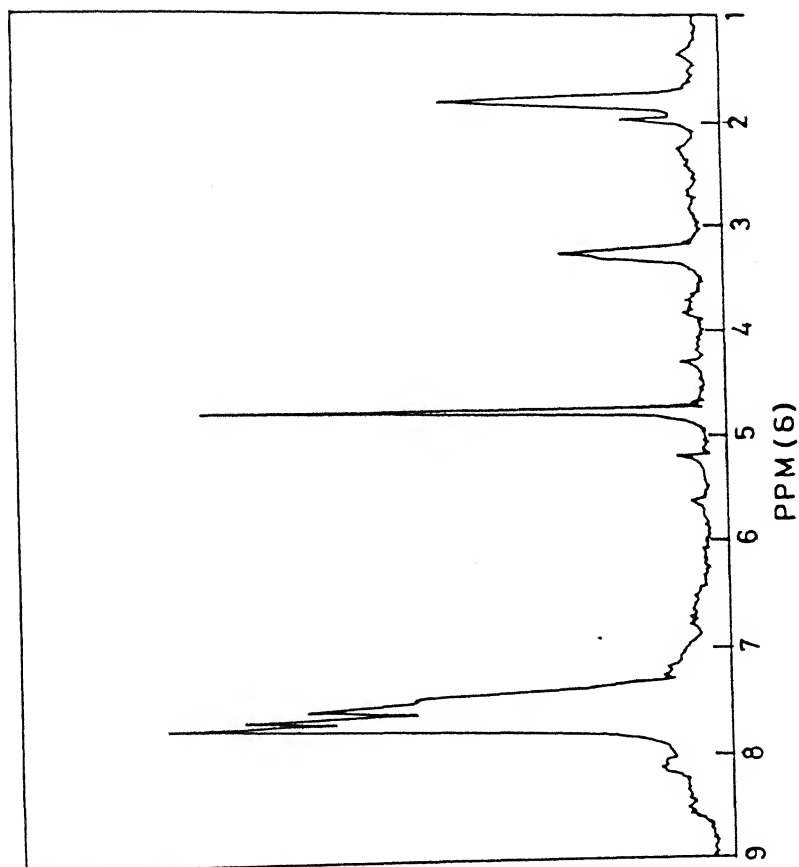


Fig.V.3. ^1H NMR Spectrum of
 $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10}\text{N}_2)]\text{PF}_6$

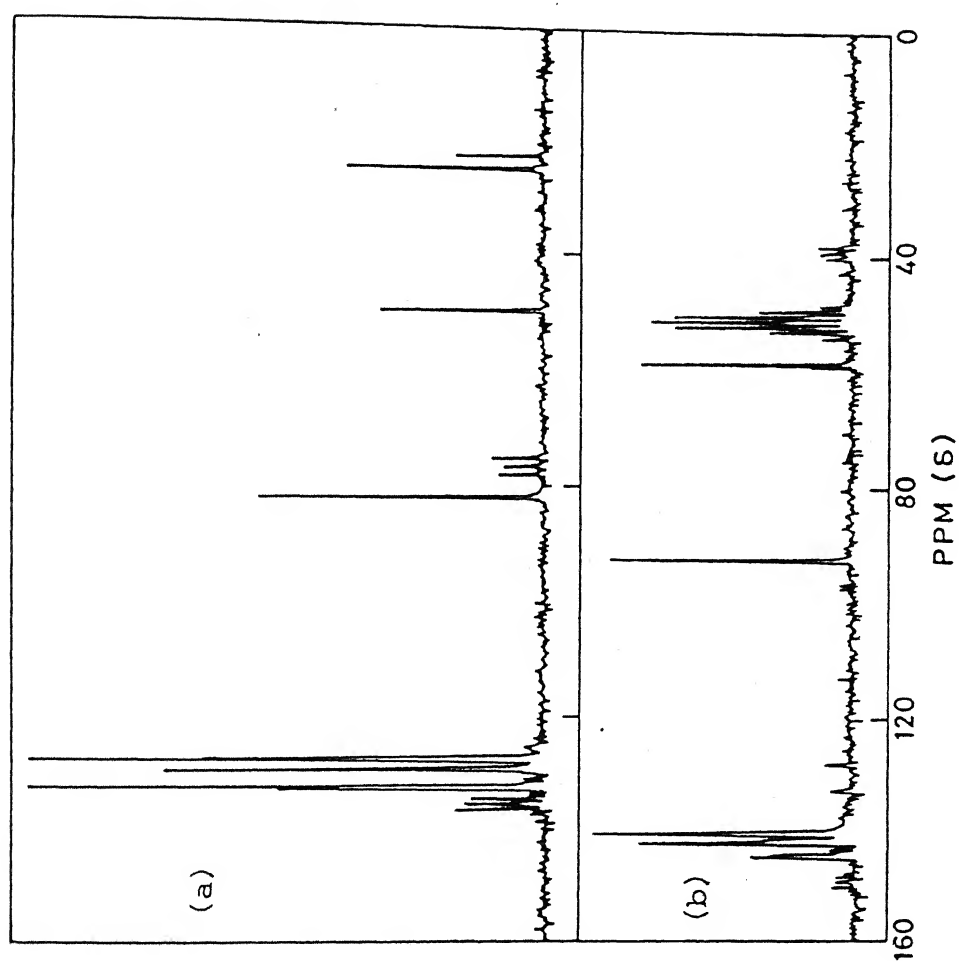


Fig. IV.4. ^{13}C NMR spectra of

(a) $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10}\text{N}_2)]\text{PF}_6$

(b) $[\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{dppe})_2(\mu\text{-C}_6\text{H}_8\text{N}_4)](\text{PF}_6)_2$

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of $-C\equiv N$ and $-N-C\equiv N$ moieties.²⁶⁻²⁸ We, therefore, wished to exploit the nucleophilicity of nitrogen atoms in these molecules in synthesizing and characterizing the metal complexes in neutral non-aqueous medium. It is likely that such a study could provide us an insight in (1) the extent of the relative nucleophilicity of various nitrogen atoms and (2) the structural behaviours of the neutral molecules in solution. This chapter (Part I) reports the reactions of cyanamide (CM) and dicyanadamide (DCDM) with $[Ru(\eta^5-C_5H_5)ClL_2]$ ($L = PPh_3, AsPh_3$ or $SbPh_3$; $L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm)). The reaction products have been characterised by elemental analyses, spectroscopic (i.r., n.m.r.) studies and conductivity measurements.

Experimental

All chemicals of Analar or chemically pure grade were used without further purification. All solvents were purified and dried.²⁹ Complexes $[Ru(\eta^5-C_5H_5)ClL_2]$ ($L = PPh_3, AsPh_3$ or $SbPh_3$; $L_2 = dppe$ or $dppm$) were prepared by literature methods.³⁰⁻³³ Analytical and spectral data of the products were obtained as described elsewhere.³²

(A) Reactions of cyanamide (CM) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$
(L = PPh_3 , AsPh_3 or SbPh_3)

A typical reaction was carried out as follows. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{EPh}_3)_2]$ (E = P, As or Sb) (0.13 mmol) and cyanamide (0.24 mmol) were taken in 30 ml of dry methanol and stirred overnight until the starting material dissolved completely. The resulting solution was filtered and NaBPh_4 (0.11 mmol) was added to the filtrate, followed by stirring for about 10 minutes. A yellow compound precipitated. It was separated by centrifugation, washed several times with methanol, ether and dried in vacuo (yield, ca. 45 %). Analyses corresponded to the formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{NH}_2\text{CN})(\text{EPh}_3)]_2(\text{BPh}_4)_2$. The hexafluorophosphate salt of the complex was obtained by a similar procedure except that NH_4PF_6 (0.12 mmol) was added in place of NaBPh_4 . The resulting orange yellow solution was stirred for 3-4 h more, filtered and evaporated to dryness. The residue was extracted with dichloromethane (5 ml) and 40 ml of petroleum ether was added to the extract. A pale yellow coloured compound precipitated which was separated, washed with petroleum ether and dried in vacuo. The complex was analysed for $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}(\text{NH}_2\text{CN})]_2(\text{PF}_6)_2$ (L = PPh_3 , AsPh_3 or SbPh_3) (yield, ca. 38 %).

Our attempts to react cyanamide with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-ClL}_2]$ ($\text{L}_2 = \text{dppe}$ or dppm) were unsuccessful.

- (B) Reactions of dicyanadiamide (DCDM) with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$
(L = PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) in presence
of a suitable anion

The complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ (0.13 mmol) was suspended in dry methanol (25 ml) containing a salt of a suitable anion (NH_4PF_6 or NaBPh_4) (0.25 mmol) and dicyanadiamide (0.12 mmol). The resulting mixture was refluxed for about 2 h whereby $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ started to dissolve slowly and bright yellow shiny crystals of the complex appeared. These were separated by centrifugation. More crystals were obtained by slow concentration of the centrifugate on a waterbath. The crystals were washed with methanol, diethyl ether, light petroleum ether and dried under vacuum (yield, ca. 40%). Analyses corresponded to a formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)\text{L}_2]\text{X}$ (L = PPh_3 , AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; X = PF_6^- or BPh_4^-).

The same reaction when carried out in the absence of anion gave a bright yellow clear solution after refluxing the starting materials for about two hours. The solution was evaporated to dryness under reduced pressure. The yellow residue was extracted with benzene. 45 ml of petroleum ether was added to the extract. A yellow complex precipitated out which was separated by centrifugation, washed several times with petroleum ether and dried in vacuo. The analyses of the yellow powdered complex corresponded to the formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)\text{L}_2]\text{Cl.HCl}$ (yield, ca. 45%).

Results and Discussion

Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with cyanamide and dicyanadiazide yielded bright yellow cationic mono/di nuclear complexes in presence of a suitable anion (Cl^- , PF_6^- or BPh_4^-). The reactions of CM with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{dppe}/\text{dppm})]$ were unsuccessful. Microanalytical data suggested their formulae given in Table VI.1. They are non-hygroscopic. The chloro salts are highly soluble in dichloromethane, chloroform, methanol, benzene, DMSO and insoluble in light petroleum or diethyl ether. The hexafluorophosphate and tetraphenylborate salts of dicyanadiazide are moderately soluble in chloroform, dichloromethane and acetone, highly soluble in DMSO, DMF and insoluble in methanol, petroleum ether or diethyl ether. The hexafluorophosphate salt of cyanamide is readily soluble in chloroform. CH_2Cl_2 whereas BPh_4 salt is insoluble in these solvents.

The most distinctive feature of the CM derivatives from those of DCDM ones is their formulation. In CM derivatives one PPh_3 molecule and the Cl^- ion are substituted by one molecule of cyanamide thus suggesting it acting as a bidentate ligand towards either one or two metal ions, while in dicyanadiazide complexes only Cl^- is substituted by one molecule of DCDM implying monodentacy of the ligand. It has been shown earlier that both

nitrogen atoms of $\text{H}_2\text{N}^2-\text{C}\equiv\text{N}^1$ are quite basic, N^1 being more than N^2 . One would therefore expect the participation of both the nitrogen atoms in coordinate bond formation with the metal ions. In the case of DCDM it has been demonstrated that the molecule (DCDM) exists mostly in the amino form $[(\text{NH}_2)^{3,4}_2\text{CN}^2\text{CN}^1]$ rather than in the imino form $(\text{NH}_2)\text{C}(=\text{NHN})\text{CN}$ with considerable negative charge on N^1 (-0.48) and N^2 (-0.44) and thus making the nitrogens N^3 , N^4 less basic for effective coordination. It seems that by donating a lone pair to the metal atom by the cyano group effectively reduces the availability of amino nitrogen lone pair for coordination. Furthermore the i.r. spectral data also suggested a strong delocalization of the electron pair of N^2 over N^1 , C^1 and N^2 centres resulting in the increase of the N^2-C^1 bond order. Presumably as a result of coordination through nitrile group, the state of delocalization has become more favourable and effective for the lone pair on N^2 .

Dibasic nature of cyanamide ligand is also supported by the failure of our attempts to react it with dppe and dppm complexes $[\text{Ru}(\eta^5-\text{C}_5\text{H}_5)(\text{dppe/dppm})\text{Cl}]$. In the latter complexes, dppe or dppm forms chelate ring with ruthenium and presumably opening up this ring in order to form two separate bonds through CM (bidentate) is energetically unfavourable.

Another interesting aspect of these interactions is the ligand coordination in the neutral state suggesting the formation of their anions to be difficult in the neutral medium.

The distinction between the charges on the cationic species of CM and DCDM complexes has been made by the conductivity measurements in highly pure and dry methanol according to a procedure adopted by Feltham and Hayter.³⁴ From the values of measured equivalent conductance in the concentration range 10^{-2} - 10^{-4} equiv. lit.⁻¹ the equivalent conductance at infinite dilution (λ_0) was determined by extrapolation. Subsequent values of ($\lambda_0 - \lambda_e$) were plotted as a function of \sqrt{c} .³⁵⁻³⁷ The slopes of the straight lines (204, 190) compared very well with the Feltham's values for 1:1 complexes and thus providing an evidence for the charge on the cation. The bonding modes in the complexes and their tentative structures have been deduced following spectral studies.

I.R. Spectra

The i.r. spectra of all the complexes display characteristic bands of all the 'spectator' ligands (EPh_3 , dppe, dppm, C_5H_5 etc.).

(a) Cyanamide Complexes

The i.r. spectra of cyanamide molecule has already been

discussed earlier in the literature.^{1-4,38} The model considered for the interpretation of the spectra of its complexes is assumed to be amide nitrile ($\text{H}_2\text{N}-\text{C}\equiv\text{N}$).^{1,3} There is a very little possibility of its existing in the form of amide isonitrile ($\text{H}_2\text{N}-\text{N}\equiv\text{C}$) or gauche carbodiimide ($\text{HN}=\text{C}=\text{NH}$) except for the contribution of the latter as one of the resonating structures where the lone pair on N^2 participates in the delocalization process with separation of charges ($\text{H}_2\text{N}=\text{C}=\text{N}$). Accordingly the cyanamide complexes should display bands due to $\nu \text{C}\equiv\text{N}$, $\nu_{\text{as}}(\text{NH}_2)$, $\nu_{\text{sym}}(\text{NH}_2)$, $\text{HN}-\text{N}$ scissor, $\nu_{\text{sy}}(\text{NCN})$, NH_2 twist, NH_2 rock (δNCN) and $\tau(\text{NCN})$ around 2250 cm^{-1} , 3300 cm^{-1} , 1600 cm^{-1} , 1200 cm^{-1} , 950 cm^{-1} , 850 cm^{-1} , 575 cm^{-1} and 450 cm^{-1} respectively.¹ In the carbodiimide model the rocking and twisting modes of NH_2 group would have no counterparts. The distinction between the spectra of the nitrile and isonitrile forms of cyanamide will necessarily lie in the differences in the skeletal frequencies of the $>\text{N}-\text{C}\equiv\text{N}$ and $>\text{N}-\text{N}\equiv\text{C}$ groups. The position of $\nu(\text{C}\equiv\text{N})$ in isonitrile (ca. 2100 cm^{-1}) has generally been found to occur about 100 cm^{-1} lower than in the corresponding nitrile form (ca. 2250 cm^{-1}). Besides, $\nu(\text{N}-\text{N})$ in isonitrile should occur below 1000 cm^{-1} while $\nu(\text{C}-\text{N})$ in nitriles around 1200 cm^{-1} . In addition if the lone pair on amino nitrogen is delocalized over $\text{N}-\text{C}-\text{N}$ moiety on coordination, the position of $\nu_{\text{sy}}(\text{N}-\text{C}-\text{N})$ should shift towards higher frequency because of the increase in $>\text{N}-\text{C}$ bond order.

The data (Table VI.1) confirms the model which we have presumed. The cyanamide complexes exhibited bands due to $\nu \text{ C}\equiv\text{N}$, $\nu_{\text{as}}(\text{NH}_2)$ and $\nu_{\text{sy}}(\text{NH}_2)$ at 2280 cm^{-1} , 3400 cm^{-1} , 3305 cm^{-1} respectively (Fig. VI.1). These occurred at higher frequencies compared to those present in the spectrum of cyanamide (2264 , 3300 and 3215 cm^{-1}). The positive shifts in these positions as a result of coordination indicate that both the cyano and the NH_2 groups are coordinated to the metal centre. It is then concluded that the coordination of the metal ions in cyanamide complexes is through nitrile and amino nitrogen and the ligand is present as $\text{H}_2\text{N}-\text{C}\equiv\text{N}$.

(b) Dicyanadiamide Complexes

The i.r. spectra of the dicyanadiamide complexes showed several bands in the region $3000\text{--}3350 \text{ cm}^{-1}$ attributed to $\nu_{\text{N-H}}$ of the amide groups and no splitting or shifting of these bands were found. However the bands broadened as compared to that in the free ligand, indicating that the nitrogen of the amide groups were not likely to be involved in bonding with ruthenium metal. $\nu(\text{C}\equiv\text{N})$ bands in the complexes appeared in form of one sharp band at 2260 cm^{-1} and another of medium to weak intensity at 2220 cm^{-1} (Fig. VI.2). These were found to be shifted towards a higher frequency region with respect to that in the free dicyanadiamide ligand (ca. 2170 cm^{-1} and 2220 cm^{-1}), the shift implies direct coordination of ruthenium to the cyano nitrogen of the

ligand. Band characteristic of $\text{N}-\text{C}\equiv\text{N}$ skeleton in free DCDM ligand ($\text{ca. } 1255 \text{ cm}^{-1}$) was also found to be shifted towards high frequency side, $\text{ca. } 1280 \text{ cm}^{-1}$. It not only indicated a metal to nitrile nitrogen coordination, but also suggested that the coordination promotes the effective overlap of the amine lone pair on N^2 with the p-orbitals on nitrile carbon atom imparting an increase in the double bond character between amino nitrogen and cyano carbon. It appears that as a result of coordination through nitrile group, the state of delocalized lone pair electron has become more favourable and effective. Thus despite the presence of negative charge on N^2 ($\text{>N}^2-\text{C}^1\equiv\text{N}^1$), the lone pair on N^2 nitrogen does not involve itself in coordination but prefers to be delocalised over $\text{N}-\text{C}-\text{N}$ group resulting in a considerable gain in delocalization energy. Interestingly the position of $\nu(\text{C}\equiv\text{N})$ in CM complexes also is on the higher energy side (2280 cm^{-1}) compared to that in DCDM complexes (2260 cm^{-1}) which further gave a support to the fact that the lone pair of electrons on N^2 in DCDM complexes is involved in the delocalization process resulting in the increase in contribution of $-\text{N}=\text{C}=\text{N}$ among its various resonating structures and thus reducing the bond order of $\text{C}\equiv\text{N}$.

In the complexes of both the ligands the position of $\nu(\text{C}\equiv\text{N})$ band shift towards higher wave numbers which indicates the absence of π -back bonding from the metal to the nitrile group.

There is a distinct splitting of a $\nu(\text{C}\equiv\text{N})$ band in the spectra of the complexes. This may be because of the Fermi resonance between $\nu(\text{C}\equiv\text{N})$ and the overtone frequency involving $\nu(\text{C}-\text{N})$ stretch. In addition, $\nu(\text{NH}_2)$ bands in the spectra of cyanamide complex are relatively more sharp compared to those in the ligand. This could arise because of the decrease in the extent of inter/intramolecular hydrogen bonding in the complexes.

N.M.R. Spectra

The n.m.r. spectra of cyanamide complexes show signals at δ 4.4 ppm (C_5H_5), δ 4.7 ppm (NH_2) (Fig. VI.3). The C_5H_5 protons resonate at a down field value compared to the C_5H_5 protons in the starting complexes (ca. δ 4.1). The phenyl protons in the complexes resonated as broad multiplets in the expected region (δ 7.0-7.6). ^{13}C n.m.r. spectra of these complexes exhibited C_5H_5 carbon at around δ 87.4 which was found to be shifted considerably downfield as compared to the C_5H_5 band found in the starting complexes (ca. δ 82.0 ppm). The phenyl carbons exhibited sharp multiplets in the expected region (δ 128.0-140.9). There is no peak present in the region δ 120 ppm due to carbon of $\text{C}\equiv\text{N}$ but it has shifted to downfield side and is present around δ 126.7 ppm (Fig. VI.4).

The $\eta^5\text{-C}_5\text{H}_5$ protons in the ^1H n.m.r. of dicyanadiamide complexes exhibited a singlet at δ 4.3 with EPh_3 ($\text{E} = \text{P}, \text{As}$) as

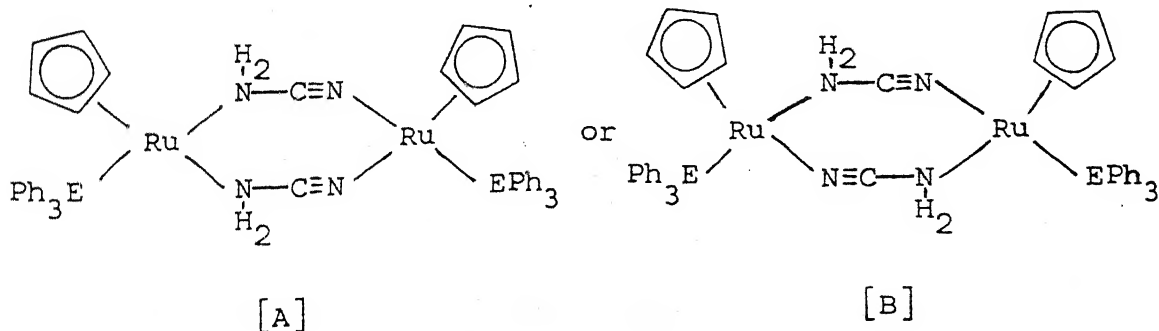
coligands and at δ 4.6 with dppe/dppm as coligands (Fig. VI.3). The NH protons exhibited a broad peak at around δ 3.4 ppm. The phenyl protons appeared around δ 7.0-7.8 (br multiplet). ^{13}C n.m.r. spectra of complexes exhibited C_5H_5 carbons at δ 82.3, $\text{C}\equiv\text{N}$ carbon at δ 122.0 and $(\text{NH}_2)_2\text{-C}\equiv\text{N}$ carbon, at δ 162.8. The phenyl carbons resonated as sharp multiplets in the region δ 128.0-137.0 ppm (Fig. VI.4).

^{13}C n.m.r. data showed deshielding of carbon atom in the $-\text{N}-\text{C}\equiv\text{N}$ moiety in the complexes of both ligands. It could be that on complexation of nitrile nitrogen to ruthenium, the electron density on carbon of $\text{C}\equiv\text{N}$ group is polarised towards nitrogen resulting in deshielding of carbon nucleus. It further appears that the deshielding in cyanamide complexes is more relative to that in dicyanadiamide ones.

The distinction between the involvement or non involvement of lone pair on N^2 ($-\ddot{\text{N}}^2-\text{C}^1\equiv\text{N}^1$) on coordination to the metal centre, and resonance over the moiety $-\text{N}-\text{C}\equiv\text{N}$ could be obtained from the extent of deshielding of nitrile carbon. In case of involvement in the resonance, the possibility of deshielding should be much less because of the polarization of the lone pair of electrons towards carbon and vice versa. Furthermore the coordination of N^2 nitrogen to the metal centre, should deshield the carbon centre more one should therefore expect less deshielding in dicyanadiamide complexes (δ 122.0) compared to

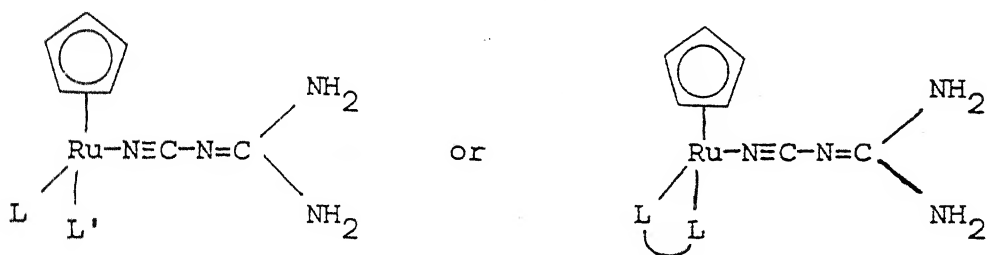
that in the cyanamide ones, which further supports the conclusions drawn from i.r. studies that in DCDM complexes the lone pair on N^2 is partially delocalized over $\ddot{N}-C\equiv N$, while in those of cyanamide, it is involved in coordination with ruthenium. Another worth noting point is the presence of a single sharp peak of C_5H_5 protons and carbon in the spectra of cyanamide complexes which indicates the two equivalent ruthenium centres when the ligand is assumed to be acting as bidentate towards two metal centres.

Based on the above spectral, analytical and conductivity data, it appears certain that the metal is coordinated through nitrogen of cyano group of both the ligands. In CM complexes besides the coordination of CN group with the metal center, the ligand binds through its second nitrogen atom (N^2) also and thus acting as a bidentate. In the latter complexes the ligand may act as bidentate towards two metal ions or one metal ion. Its bidentacy towards one metal ion is ruled out on the ground of great strain present in the highly unstable four membered ring formed by the ligand and thus its bidentacy towards two metal ions is preferred.



The molecules may have two isomers A and B. The electron density on two ruthenium centres in isomer A is not equivalent which should result in two isomer shifts of protons and ^{13}C carbons of C_5H_5 molecule, since one resonance peak is observed for the protons and ^{13}C in the proton and ^{13}C n.m.r. spectra, the structure [B] is preferred over [A].

For the complexes of DCDM, the following structure is proposed.



$\text{L}, \text{L}' = \text{PPh}_3, \text{AsPh}_3 \text{ or } \text{SbPh}_3$

$\text{L-L} = \text{dppe or dppm}$

Table VI.1. Analytical and Spectral Data of the Complexes.

S.No.	Complexes	Colour (m.p./°C)	Found (calcd) %			Major I.R. band (cm ⁻¹)	¹ H N.M.R. C ₅ H ₅ (δ ppm)	¹³ C N.M. C ₅ H ₅ (δ)
			C	H	N			
1	2	3	4			5	6	7
1.	[Ru(η ⁵ -C ₅ H ₅)(PPh ₃)(NH ₂ CN)] ₂ (PF ₆) ₂	YG (140)	47.1 (46.8)	3.3 (3.6)	4.0 (4.5)	2280	4.4	87.4
2.	[Ru(η ⁵ -C ₅ H ₅)(PPh ₃)(NH ₂ CN)] ₂ (BPh ₄) ₂	Y (162)	72.9 (73.0)	5.2 (5.3)	3.9 (3.5)	2290	4.46	87.5
3.	[Ru(η ⁵ -C ₅ H ₅)(AsPh ₃)(NH ₂ CN)] ₂ (PF ₆) ₂	YG (145)	43.1 (43.7)	3.9 (3.3)	4.0 (4.2)	2285	4.4	87.4
4.	[Ru(η ⁵ -C ₅ H ₅)(AsPh ₃)(NH ₂ CN)] ₂ (BPh ₄) ₂	Y (152)	68.5 (69.1)	5.1 (5.0)	3.1 (3.3)	2280	4.5	87.6
5.	[Ru(η ⁵ -C ₅ H ₅)(SbPh ₃)(NH ₂ CN)] ₂ (PF ₆) ₂	YG (143-145)	41.4 (40.8)	3.8 (3.1)	4.2 (4.9)	2280	4.4	87.4
6.	[Ru(η ⁵ -C ₅ H ₅)(SbPh ₃)(NH ₂ CN)] ₂ (BPh ₄) ₂	YG (158)	65.7 (65.4)	4.8 (4.7)	4.1 (3.2)	2290	4.4	87.5
7.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(PPh ₃) ₂][Cl.HCl]	Y (120)	60.6 (60.9)	5.2 (4.7)	6.8 (6.6)	2260	4.3	82.3
8.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(PPh ₃) ₂][PF ₆]	Y (160)	56.7 (56.1)	4.8 (4.2)	5.8 (6.1)	2260	4.3	82.5
9.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(PPh ₃) ₂][BPh ₄]	Y (170-175)	73.3 (73.5)	5.2 (5.4)	5.5 (5.1)	2265	4.34	82.3
10.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(AsPh ₃)(PPh ₃)]Cl.HCl	Y (125)	58.2 (57.9)	4.3 (4.4)	7.7 (7.2)	2258	4.32	82.3
11.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(AsPh ₃)(PPh ₃)]PF ₆	Y (157)	53.9 (53.6)	4.4 (4.0)	5.3 (5.8)	2265	4.3	82.4
12.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(AsPh ₃)(PPh ₃)]BPh ₄	Y (172)	71.4 (70.7)	5.8 (5.2)	5.3 (4.9)	2260	4.32	82.4
13.	[Ru(η ⁵ -C ₅ H ₅)(C ₂ H ₄ N ₄)(AsPh ₃) ₂][Cl.HCl]	Y (115-120)	56.0 (55.2)	4.5 (4.3)	5.0 (5.9)	2265	4.4	82.6

...contd.

Table VI.1 (contd.)

1	2	3	4	5	6	7			
14.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{AsPh}_3)_2]\text{PF}_6$	$\bar{\gamma}$ (158-160)	51.9 (51.2)	3.5 (3.9)	5.6 (5.5)	-	2260	4.38	82.4
15.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{AsPh}_3)_2]\text{BPh}_4$	$\bar{\gamma}$ (168)	68.8 (68.1)	5.4 (4.9)	5.1 (4.7)	-	2265	4.32	82.3
16.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{SbPh}_3)_2]\text{Cl.HCl}$	$\bar{\gamma}$ (128)	50.6 (50.1)	4.2 (3.9)	5.7 (5.4)	6.2 (6.9)	2260	4.4	83.0
17.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{SbPh}_3)_2]\text{PF}_6$	$\bar{\gamma}$ (155)	46.7 (46.9)	3.6 (3.5)	5.2 (5.1)	-	2260	4.38	83.2
18.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{SbPh}_3)_2]\text{BPh}_4$	$\bar{\gamma}$ (100)	63.5 (63.0)	4.4 (4.6)	4.5 (4.4)	-	2258	4.36	82.6
19.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppe})]\text{Cl.HCl}$	$\bar{\gamma}$ (132-135)	54.2 (55.0)	4.8 (4.7)	7.4 (7.7)	8.9 (9.8)	2265	4.6	82.4
20.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppe})]\text{PF}_6$	$\bar{\gamma}$ (158)	50.9 (50.0)	4.9 (4.2)	7.8 (7.1)	-	2260	4.6	82.4
21.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppe})]\text{BPh}_4$	$\bar{\gamma}$ (155)	71.4 (70.8)	5.9 (5.5)	6.2 (5.8)	-	2258	4.65	82.3
22.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppm})]\text{Cl.HCl}$	$\bar{\gamma}$ (130)	54.8 (54.4)	4.9 (4.5)	7.2 (7.9)	9.2 (10.0)	2260	4.7	82.5
23.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppm})]\text{PF}_6$	$\bar{\gamma}$ (148-151)	50.1 (49.4)	4.3 (3.8)	7.7 (7.2)	-	2260	4.72	82.5
24.	$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4\text{N}_4)(\text{dppm})]\text{BPh}_4$	$\bar{\gamma}$ (154)	70.9 (70.5)	6.0 (5.2)	6.2 (5.8)	-	2265	4.6	82.3

γ =yellow, γ_3 =yellowish green, dppe=1,2-bis(diphenylphosphinoethane), dppm=1,2-bis(diphenylphosphinoethane).

Infra Red Spectra of the Complexes

- Fig. VI.1. (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NH}_2\text{CN})]_2(\text{PF}_6)_2$
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NH}_2\text{CN})]_2(\text{BPh}_4)_2$

- Fig. VI.2. (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)(\text{PPh}_3)_2]\text{Cl.HCl}$
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)(\text{AsPh}_3)_2]\text{PF}_6$
 (c) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)\text{dppe}]\text{Cl.HCl}$

Fig. VI.3. ^1H NMR Spectra of the Complexes

- (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NH}_2\text{CN})]_2(\text{PF}_6)_2$
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NH}_2\text{CN})]_2(\text{BPh}_4)_2$
 (c) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)(\text{PPh}_3)_2]\text{BPh}_4$
 (d) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)\text{dppm}]\text{BPh}_4$

Fig. VI.4. ^{13}C NMR Spectra of the Complexes

- (a) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NH}_2\text{CN})(\text{AsPh}_3)]_2(\text{BPh}_4)_2$
 (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)(\text{PPh}_3)_2]\text{Cl.HCl}$
 (c) $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)\text{dppe}]\text{Cl.HCl}$

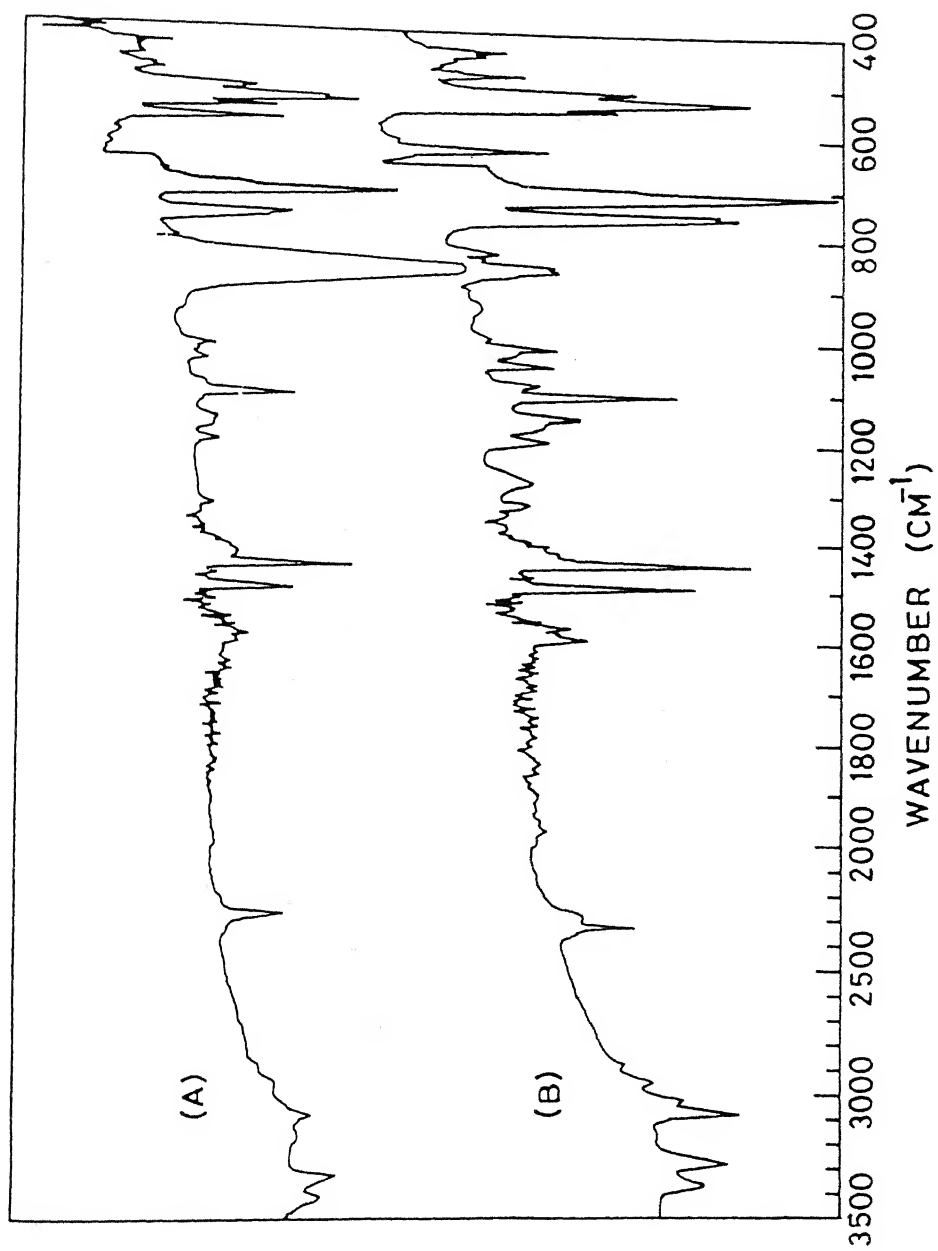


Fig. VI.1

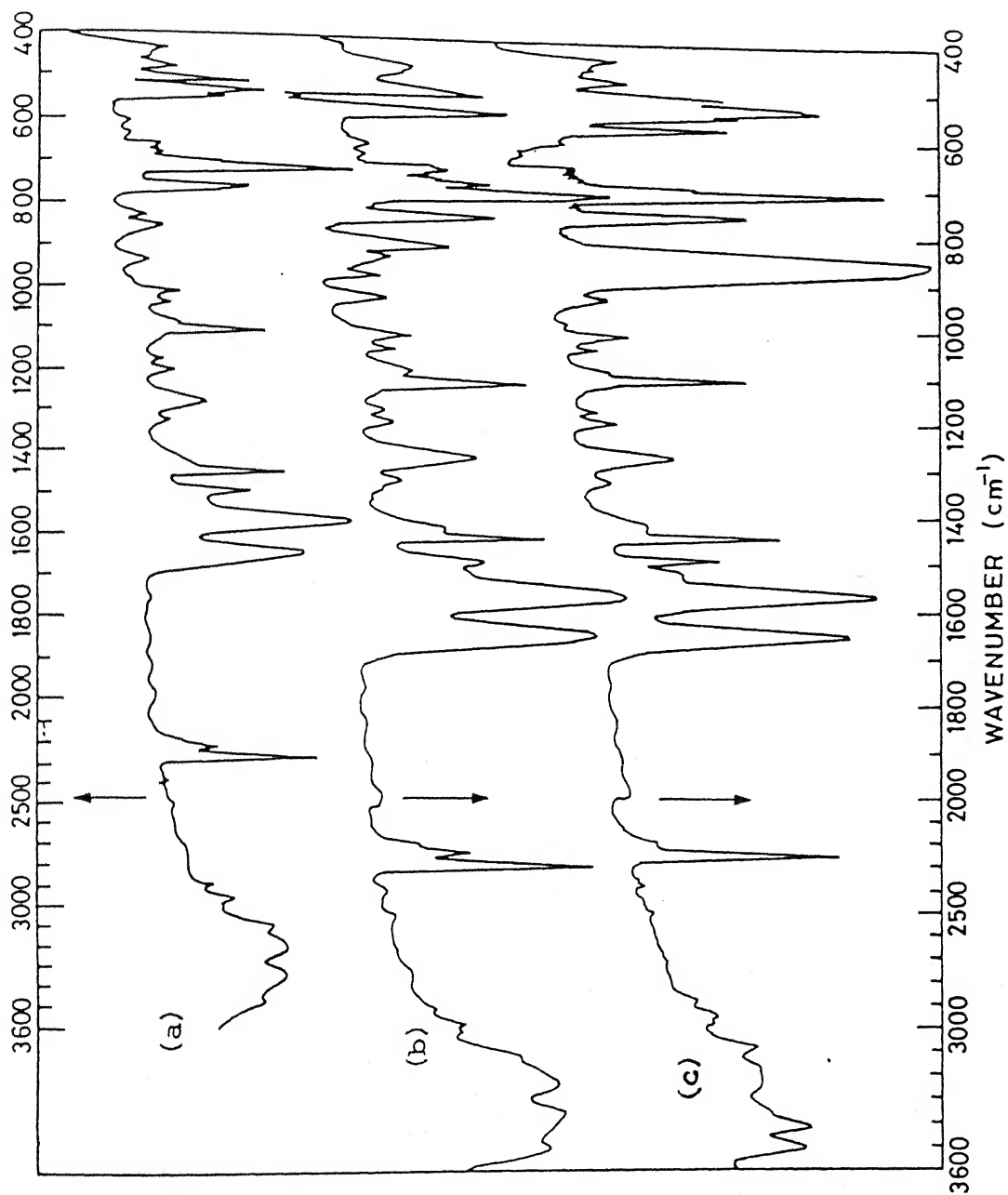


Fig.VI.2

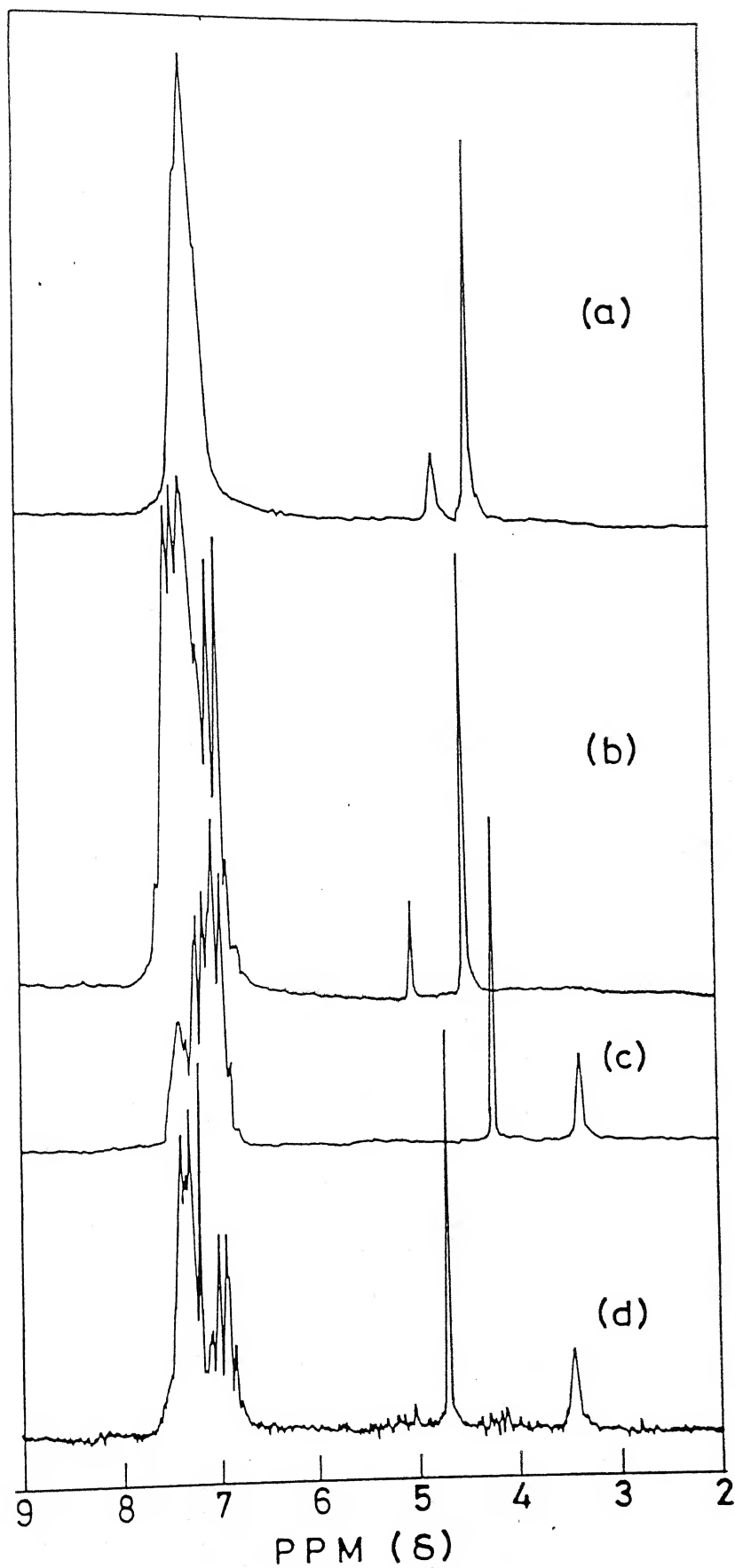


Fig. VI.3

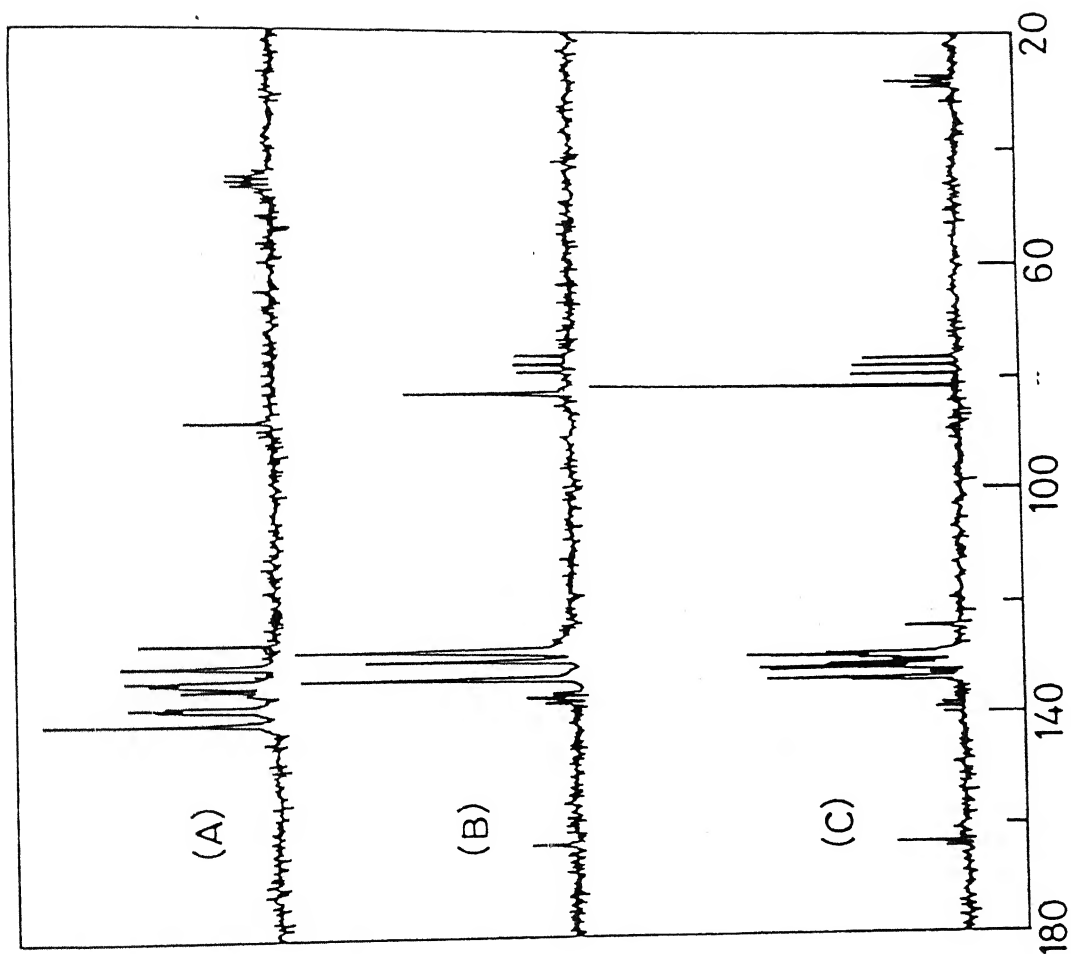


Fig. VI.4

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CHAPTER VI

Part II: A NEW ROUTE FOR SYNTHESIS OF $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\mu\text{-CN})\text{RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]^+\text{X}^-$ ($\text{L}, \text{L}' = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2, \text{L}_2' = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ or $\text{PPh}_2\text{CH}_2\text{PPh}_2$, $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$ or BPh_4^-) USING 1,3,5-TRIAZINE

Introduction

Most of the properties of the aromatic, resonance stabilised 1,3,5-triazine, highly unstable in presence of a base like H_2O , ROH or NH_3 are determined by the difference in the electron density on N and C atoms of the ring.¹⁻⁸ Its dissociation into HCN is highly improbable under usual experimental conditions.^{1,2} The nucleophilicity of the nitrogen atoms could be utilized to provide a general route to synthesise trinuclear triazine bridged complexes by its interaction with the metal complexes. In case the reactions are carried out in OH containing solvents, a competitive hydrolysis reaction of 1,3,5-triazine may lead to formation of either a formato or/and formamido complexes.³ Under ordinary reaction conditions, cyano- or/and cyano- bridged bimetallic complexes are highly unexpected. In this chapter (Part II) we wish to report the first example where triazine molecule has been completely dissociated. As a result of this depolymerization a novel and unusual one pot synthesis of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\mu\text{-CN})\text{RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]^+\text{X}^-$ ($\text{L}, \text{L}' = \text{PPh}_3,$

AsPh₃ or SbPh₃; L₂, L₂' = dppe or dppm; X⁻ = PF₆⁻, BF₄⁻, BPh₄⁻) by the interaction of [Ru(η⁵-C₅H₅)L₂X] (L = PPh₃, AsPh₃ or SbPh₃; L₂ = dppe or dppm; X = Cl, Br or H) with 1,3,5-triazine in methanol has been developed which is reported in this chapter. Similar reactions were also carried out using [Ru(Bipy)₂-Cl₂] where formation of the formamidino complexes of ruthenium has been suggested. These reactions have also been carried out in other -OH containing solvents.

Experimental

The following example is representative of the reactions carried out.

To a suspension of [Ru(η⁵-C₅H₅)L₂X] (L = PPh₃, AsPh₃ or SbPh₃; L₂ = dppe or dppm; X = Cl, Br or H) (0.13 mmol) in methanol (30 ml) was added the salt of a suitable anion (NaBF₄, NH₄PF₆ or NaBPh₄) (0.25 mmol) and 1,3,5-triazine (0.40 mmol). It was stirred for a couple of minutes and the subsequent mixture was heated to reflux for about fifteen hours. Initially the colour of the solution changed to deep red which finally faded to orange or light yellowish orange colour and all the suspended material went into solution. The clear refluxed solution was concentrated on a waterbath whereupon bright yellow shining crystals separated out. (In some cases the yellow crystals were separated out from the solution during refluxing period. In those cases the solution was not concentrated). The crystals

were separated by centrifugation, washed several times with methanol, ether and dried in vacuum (yield, ca. 60 %). They were analysed for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\mu\text{-CN})\text{RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]^+\text{X}^-$ ($\text{L}, \text{L}' = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2, \text{L}_2' = \text{dppe}$ or dppm ; $\text{X}^- = \text{PF}_6^-, \text{BF}_4^-$ or BPh_4^-) (Table VI.2).

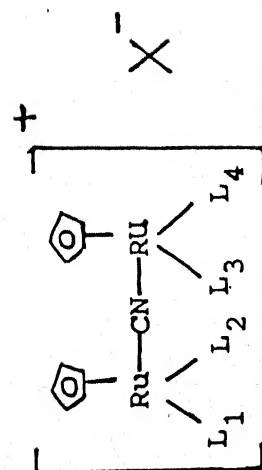
Results and Discussion

The final crystalline products were confirmed by various physico chemical techniques (microanalysis, m.p., mixed m.p., i.r., ^1H , ^{31}P , ^{13}C n.m.r., electronic spectra, X-ray powder pattern) and comparing them with those of the authentic samples obtained from literature methods.^{9,10} These were further confirmed by carrying out their reactions described in the literature.¹⁰

Our initial experiments of the interaction of 1,3,5-triazine with other systems like $[\text{Ru}(\text{bipy})_2\text{X}_2]$ ($\text{X}=\text{Cl}$) in alcohols suggested that the former gets initially hydrolysed with the formation of either buff or red coloured formato or formamidino complexes. These have been separated and analysed. We therefore speculate that the red coloured complex formed initially during the reaction is possibly formamidino complex of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}]^+$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) system coordinated as monodentate. The latter on refluxing dissociates releasing one mole of NH_3 and the resulting product subsequently interacts

with another mole of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2]^+$ forming a more stable CN bridged complex. The work on this and other reactions is under progress.

Table VI.2. Characterisation Data of the Complexes



Sl. No.	Ligands				Anion	Colour, M.P. (°C) Yield %	I.R. (cm ⁻¹)	¹ H NMR		Analyses			³¹ P { ¹ H} nmy
	L ₁	L ₂	L ₃	L ₄				⁵ -C ₅ H ₅		Found (calcd), %			
1	2				3	4	5	1	2	7			8
1.	P	P	P	P	PF ₆	Y, (178-180) 60%	2080	4.19	4.05	63.8 (64.2)	4.22 (4.51)	0.87 (0.9)	47.3 41.6
2.	P	P	P	P	BF ₄	Y, (148) 56%	2060	4.18	4.06	67.3 (67.5)	4.8 (4.7)	1.12 (0.93)	47.4 41.5
3.	P	P	P	P	BPh ₄	Y, (152) 61%	2085	4.18	4.05	74.1 (74.4)	5.6 (5.2)	0.79 (0.81)	47.6 41.6
4.	A	P	A	P	PF ₆	Y, (175) 59%	2080	4.19	4.06	60.1 (60.7)	4.5 (4.27)	0.90 (0.85)	46.9 40.8
5.	A	P	A	P	BF ₄	Y, (153) 58%	2080	4.18	4.05	62.6 (63.75)	4.7 (4.4)	1.21 (0.88)	47.0 40.6
6.	A	P	A	P	BPh ₄	Y, (155) 62%	2090	4.20	4.07	71.0 (70.8)	4.7 (4.96)	0.72 (0.77)	46.8 40.7
7.	A	A	A	A	PF ₆	Y, (172-175) 60%	2090	4.20	4.08	58.0 (57.6)	4.12 (4.05)	0.88 (0.81)	
8.	A	A	A	A	BF ₄	Y, (152) 58%	2070	4.18	4.06	60.1 (60.4)	4.51 (4.2)	1.1 (0.8)	

Table VI.2(contd.)

1	2	3	4	5	6	7	8		
9.	A	A	A	2080	4.18	4.07	67.9 (67.5)	4.3 (4.73)	0.69 (0.73)
10.	Sb	Sb	Sb	2085	4.36 4.22	4.10 4.08	52.8 (52.0)	3.7 (3.65)	0.78 (0.73)
11.	Sb	Sb	Sb	2070	4.33 4.21	4.09 3.9	54.1 (54.3)	3.51 (3.76)	1.2 (0.75)
12.	Sb	Sb	Sb	2085	4.35 4.22	4.09 4.0	61.2 (61.5)	4.6 (4.3)	0.70 (0.67)
13.	dppe	dppe	PF ₆	2110	4.35	4.17	57.2 (58.2)	4.53 (4.45)	1.16 (1.1)
14.	dppe	dppe	BF ₄	2100	4.36	4.15	60.3 (60.9)	4.3 (4.67)	1.18 (1.12)
15.	dppe	dppe	BPh ₄	2090	4.35	4.16	70.2 (70.9)	5.6 (5.29)	1.01 (0.95)
16.	dppm	dppm	PF ₆	2090	4.30	4.16	57.1 (57.6)	4.6 (4.24)	1.2 (1.1)
17.	dppm	dppm	BF ₄	2100	4.32	4.15	60.9 (60.3)	4.7 (4.45)	1.19 (1.15)
18.	dppm	dppm	BPh ₄	2100	4.30	4.17	71.0 (70.6)	5.2 (5.1)	0.90 (0.96)
									82.1 79.7
									81.8 78.1

^a p=PPh₃, A=AsPh₃, Sb=SbPh₃, dppe=1,2-Bis(diphenylphosphino)ethane and dppm=Bis(diphenylphosphino)methane.

^b Y=Yellow.

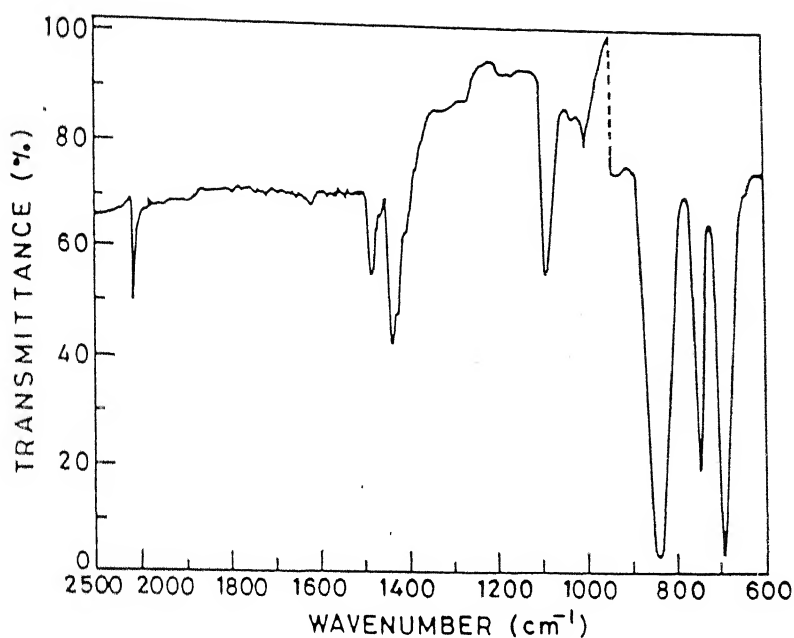


Fig.VI.5. I.R. Spectrum of the Complex

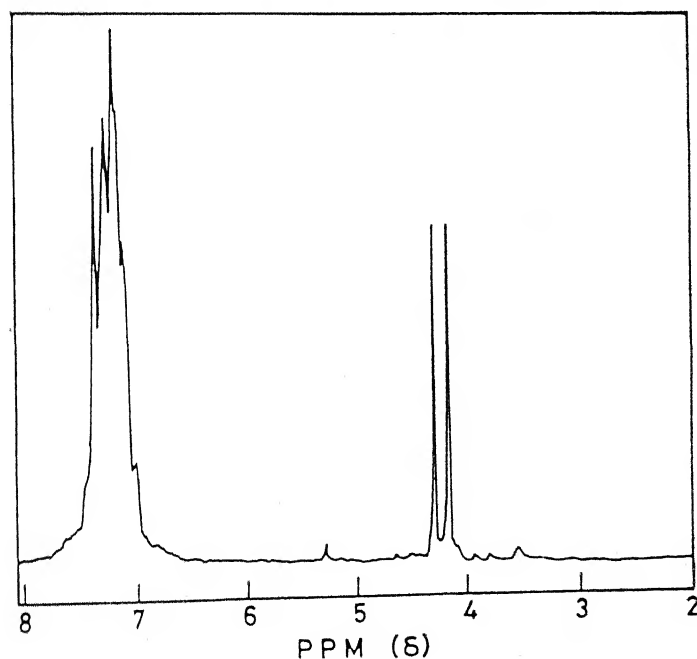
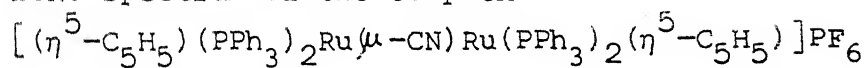
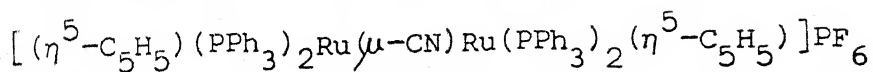


Fig. VI.6. ¹H NMR Spectrum of the Complex



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Chapter VII

SUMMARY AND SCOPE FOR FUTURE WORK

A literature survey in the past twenty years indicates the synthetic versatility and the wide horizon of unusual chemistry displayed by cyclopentadienyl bis(triphenylphosphine)ruthenium(II) complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ and its analogues. Reasons for their unusual behaviours could be (i) the high electron density on ruthenium in the complexes and (ii) the steric interactions because of the presence of two bulky PPh_3 molecules.

A concise overview of the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ first prepared by Wilkinson (1969) and later on through a facile, one step synthesis by Bruce, et al. (1977), and the scope and the objective of the work has been given in chapter one.

Chapter two describes the insertion reactions of COS and CS_2 into ruthenium hydride bond of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{H}]$ ($\text{E} = \text{P}, \text{As}$ or Sb) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{L-L})\text{H}]$ ($\text{L-L} = \text{dppe}$ or dppm) which yield monothioformato and dithioformato derivatives respectively. The mono and the dithioformate ligands in these complexes have been assumed to coordinate as monodentate. The assumption of their monodentacy character is based on the instability of the twenty electron system if these ligands behave as bidentate.

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The first and the second part of chapter three are concerned with the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with a terminal monoacetylene, 1-ethynyl pyrene and a diacetylene 1,7-octadiyne. The second part also describes the reactions of these complexes with trans 1,4-dicyano-2-butene. The reactions of 1-ethynyl pyrene yielded cationic vinylidene complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHR})\text{L}_2]\text{X}$ ($\text{R} = \text{pyrene}$; $\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X}^- = \text{BF}_4^-$, PF_6^- or BPh_4^-). These cations were readily deprotonated to give the corresponding neutral η' -ethynyl complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{R})\text{L}_1\text{L}_2]$ ($\text{R} = \text{pyrene}$, $\text{L}_1, \text{L}_2 = \text{PPh}_3$, AsPh_3 , SbPh_3 , dppe or dppm). Attempts were also made to treat the cationic and the neutral products with various alcohals.

Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ with 1,7-octadiyne in the presence of anions (BF_4^- or PF_6^-) have yielded binuclear cationic vinylidene complexes having composition $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_{10})(\text{L}_2)_2]\text{X}_2$. The corresponding neutral complexes of 1,7-octadiyne have also been synthesized by carrying out the reactions in presence of NaOMe. These complexes, (Alkynyl and Allenylidene) have been formulated as $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_8)(\text{L}_2)_2]$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_8\text{H}_6)(\text{L}_2)_2]$ ($\text{L} = \text{PPh}_3$, AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) respectively. Binuclear cationic complexes having compositions $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_6\text{H}_6\text{N}_2)(\text{L}_2)_2]\text{X}_2$ ($\text{X} = \text{BF}_4^-$ or PF_6^-) have been formed as a result of reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ with 1,4-dicyano-2-butene.

The procedures to synthesize the mononuclear and binuclear, cationic complexes by the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3$, AsPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 4-cyanopyridine and 4-cyanopyridine 1-oxide have been described in chapter four. The mononuclear complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(4\text{-CNPY})]\text{X}$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(4\text{-CNPY-O})]\text{X}$ and the binuclear complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{-Ru-4-CNPY-RuL}'_2(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{-Ru-4-CNPYO-Ru-L}'_2(\eta^5\text{-C}_5\text{H}_5)]\text{X}_2$ ($\text{L}, \text{L}' = \text{PPh}_3$ or AsPh_3 ; $\text{L}_2, \text{L}'_2 = \text{dppe}$ or dppm ; $\text{X} = \text{PF}_6^-$ or BPh_4^-) have been isolated. The charges on these species were confirmed by conductivity measurements. Besides, the i.r. and the n.m.r. studies account for the coordination through pyridine nitrogen. Strong MLCT bands in the u.v. visible spectra have been detected. These bands exhibit solvatochromic effect which has also been studied and described in this chapter.

Chapter five describes the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with piperidine-1-carbonitrile or piperazine 1,4-dicarbonitrile in the presence of a suitable anion (PF_6^- , BF_4^- , BPh_4^- or ClO_4^-). The products were found to be cationic, mono- and bi-nuclear complexes $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{L}_2)_2(\mu\text{-C}_6\text{H}_8\text{N}_4)]\text{X}_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2(\text{C}_6\text{H}_{10}\text{N}_2)]\text{X}$ ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X} = \text{PF}_6^-$, BF_4^- , BPh_4^- or ClO_4^-). The nucleophilic character of nitrogen of metal bonded cyano groups has been exploited in synthesising them.

The first part of chapter VI deals with the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with cyanamide and dicyanadiamide in the presence of a suitable anion (PF_6^- or BPh_4^-). Binuclear cationic cyanamide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NH}_2\text{CN})(\text{EPh}_3)]_2\text{X}_2$ have been isolated. Dicyanadiamide gave mononuclear cationic complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{H}_4\text{N}_4)\text{L}_2]\text{X}$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm ; $\text{X} = \text{PF}_6^-$ or BPh_4^-). The monodentacy and the bidentacy of the cyanamide and dicyanadiamide ligands have been established by the i.r. and the n.m.r. spectral studies. Second part of the chapter briefly reports a new route for the synthesis of literature reported cyano bridged cations $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Ru}(\mu\text{-CN})\text{RuL}_2'(\eta^5\text{-C}_5\text{H}_5)]^+\text{X}^-$ formed as a result of the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$ or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with 1,3,5-triazine.

Despite the large and growing literature related to the reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$, one could further extend the work already described. A few interesting problems which have the potentialities of further studies are cited below.

- (a) All the reported synthesis are, in general, carried out by substitution reactions. 'Is it possible to synthesize them starting from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ or similar ruthenium salts?'. This should be further explored.

- (b) The studies on CXY (X,Y = O,S,Se) insertion into Ru-Cl, Ru-CH₃ bonds in the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ (E = P, As, Sb; X = Cl, CH₃) can be extended. The insertion reactions of other small molecules may also be attempted.
- (c) The reactions of NOX with vinylidenes, allenylidenes acetylides will make an interesting study.
- (d) The reactions of allenylidene complexes formed by 1,7-octadiyne could be carried out with a variety of electrophilic or nucleophilic reagents. These should yield different products depending upon the site of attack on the bridging octadiyne group.
- (e) Acetylide complexes of 1-Ethynyl pyrene $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_2\text{R})(\text{EPh}_3)_2]$ (R = pyrene; E = P, As, Sb) could give rise to a wide range of new complexes by undergoing ligand exchange reactions [ligand = CO, CNBu^t, PR₃, P(OR)₃]. These may behave like a nucleophile (β-carbon, being electron rich) towards H⁺, Me⁺, alkyl halides and electrophilic olefins.
- (f) The studies related to cyanopyridine could be extended further. The complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{RuClL}_2]$ (L = PPh₃, AsPh₃; L₂ = dppe or dppm) could be allowed to react with 2- and 3-cyanopyridines. The reactions with 2-cyanopyridine may yield monomeric nitrile bound complexes in place of the pyridine bonded ones because of the steric hinderance between the cyanopyridine ring and the coligands of ruthenium-cyclopentadienyl complexes.

- (1) There is a possibility of utilizing the nucleophilic character of nitrogen in cyanide complexes for carrying out Ritter-type reactions. These could prove to be invaluable in the synthesis of new organic and inorganic compounds.

The problems, thus cited are only a few among the infinite ones. The convergence of physical and analytical techniques combined with inorganic and organic theories make this study the most exciting one. We have to combine the hard facts and the principles of inorganic discipline to understand the fascinating mysteries of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$.

List of Publications

1. Insertion reactions of carbonyl sulfide and carbon disulfide with $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2]$ ($\text{E} = \text{P, As or Sb}$).
A. Mishra and U.C. Agarwala, *Inorg. Chim. Acta*, **145**, 191-194 (1988).
2. Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{ClL}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_2 \text{ or } \text{SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$) with piperazine 1,4-dicarbonitrile or piperidine 1-carbonitrile in presence of anion (BF_4^- , PF_6^- , BPh_4^-).
A. Mishra and U.C. Agarwala, *J. Chem. Soc. Dalton Trans*, 2897 (1988).
3. Reactions of 1-Ethynyl Pyrene with Cyclopentadienyl Ruthenium Complexes.
A. Mishra, D.S. Pandey, K. Mishra and U.C. Agarwala, *Indian J. Chem.* (In press).
4. Preparation and structural properties of mononuclear and binuclear Ru(II) cyclopentadienyl complexes with 4-cyanopyridine and 4-cyanopyridine 1-oxide.
A. Mishra, K. Mishra and U.C. Agarwala, *Polyhedron* (accepted).
5. Reactivity of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3 \text{ or } \text{SbPh}_3$; $\text{L}_2 = \text{dppe or dppm}$) with 1,7-octadiyne and 1,4-Dicyano-2-butene,
A. Mishra and U.C. Agarwala, *Bull. Chem. Soc. Japan*. (communicated).

6. Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 ; $\text{L}_2 = \text{dppe}$ or dppm) with Cyanamide and Dicyanadiamide.
A. Mishra and U.C. Agarwala, *Inorg. Chim. Acta.*
(communicated).
7. A new route for the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{Ru}(\mu\text{-CN})\text{Ru}-\text{L}_2'(\eta\text{-C}_5\text{H}_5)]^+\text{X}^-$ using 1,3,5-Triazine.
A. Mishra and U.C. Agarwala, *Inorg. Chim. Acta.*
(accepted).